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EXPERIMENTAL CHEMICAL KINETICS



Editura Universității din București

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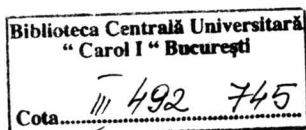
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652/12

B.C.U. "CAROL I" BUCUREȘTI



C20126711

© Editura Universității din București
Șos. Panduri, 90-92, București - 050663; Telefon/Fax: 410.23.84
E-mail: editura_unibuc@yahoo.com
Internet: www.editura.unibuc.ro

Descrierea CIP a Bibliotecii Naționale a României

Experimental chemical kinetics / Adina Răducan,

Valentin Munteanu, Mihaela Puiu, Dumitru Oancea

– București: Editura Universității din București, 2005

Bibliogr.

ISBN 973-575-977-2

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Preface

The present book, dedicated to practical works and exercises, is based on a course in chemical kinetics for chemical faculty students of the Bucharest University. It takes into consideration the main trends and prospects of classical chemical kinetics, presenting a set of experiments and solved problems at an introductory level. Since the kinetic measurements are always accompanied by significant experimental errors, a short presentation of the statistical treatment of experimental data as well as of propagation of errors was necessary. The practical works and accompanying problems are focalized over several fundamental molecular kinetic properties of matter and over the effect of different system variables like reactant concentrations, temperature, ionic strength and the presence of catalyst, promoters or inhibitors on the kinetics of some well known chemical reactions. The time evolution of the reacting systems is monitored using various procedures, from titration to physicochemical methods of analysis. Both graphical and regression methods are used for the evaluation of the kinetic parameters. The solved exercises are intended to fix the theoretical concepts and to familiarize the students with the order of magnitude of various properties. We are open to receive the observations and critics regarding the content and form of this book, which will be welcome for an improved edition.

We take this opportunity to express our gratitude to our professors who contributed decisively to the rational development of chemical kinetics in the department of physical chemistry.

The authors

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1. Treatment of Experimental Data

The experimental measurements are always affected by errors. In discussing errors in individual observations it is customary to distinguish between systematic errors and random errors.

Systematic errors are of two kinds:

a) Errors associated with the particular instruments or technique of measurement being used. For example, a balance not properly zeroed (or tarred) will provide mass values that are erroneously high or low, despite the care and competence with which the balance is read. The same is true for an uncalibrated thermometer or pressure gauge. Thus, because of the misuse or malfunctioning of the measuring instrument, all measurements are thrown off in the **same direction**. They are biased.

b) Errors, which might be referred to as a “**model error**”, are less obvious and potentially more serious than the first ones. In this case, the assumption that the system under study will behave in the predicted fashion proves to be incorrect. Suppose, for example, that a student measured the pressure – volume behavior (a hyperbola following the equation $p \cdot V = \text{constant}$). This behavior would be observed for the high-pressure measurements; the problem is the ideal gas model, which is not valid at the higher pressures. Model errors can be difficult to detect because it is often easier to mistrust your data instead to question (and analyze) the validity of the theory (model) that you are supposed to demonstrate.

Random errors – are produced by a large number of unpredictable and unknown variations in the experimental situation. They can result from small errors in judgment on the part of observer, such as in estimating tenths of the smallest scale division. Other causes are unpredictable fluctuations in conditions, such as temperature, illumination, line voltage, or any kind of mechanical vibration of the equipment. It was found empirically that such random errors are frequently distributed according to a simple law. This makes it possible to use statistical methods to deal with random errors.

The terms **accuracy** and **precision** are often used to distinguish between systematic and random errors. If a measurement has small systematic errors, we say that it has high accuracy; for small random errors, we say it has high precision.

1.1. Error Estimation

Suppose that we have n measurements of an amount x . From a statistical point of view, the real (true) value of x is the **mean** (or average) of the whole statistic population (x_0), which is formed from an infinitely large number of measurements. We define the absolute error;

$$\varepsilon_0 = x_i - x_0 \quad (1.1)$$

Generally, if we represent the frequency with which the errors appear, $f(\varepsilon)$, as a function of the magnitude of errors, we obtain a symmetrical curve with respect to Oy axis.

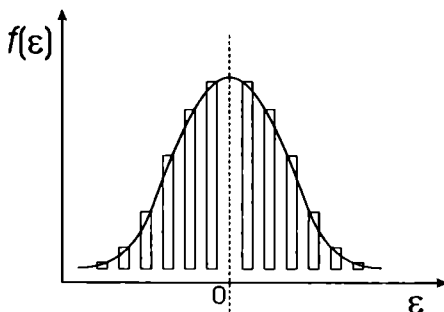


Fig. 1.1: The Gauss (normal) error distribution

This graph represents the Gauss (normal) distribution (Fig. 1.1). The $f(\varepsilon)$ function is the repartition density or the probability that the error of the measured value is ranged between ε and $\varepsilon + d\varepsilon$. The expression of the repartition density is:

$$f(\varepsilon) = \frac{h}{\sqrt{\pi}} \cdot \exp(-h^2 \cdot \varepsilon^2) \quad (1.2)$$

where h is the precision module.

1.2. The Characteristics of an Error Distribution Function

A distribution is characterized by two kinds of parameters:

a. Localization indices – give information about the central trend, symmetry and homogeneity of the considered selection. The most important indices are:

a.1 The average or the arithmetic mean – defined as the sum of all measurements divided by their number:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (1.3)$$

a.2 The geometric mean:

$$m_g = \sqrt[n]{\prod x_i} \quad (1.4)$$

a.3 The harmonic mean:

$$m_h = \frac{1}{\sum_{i=1}^n \frac{1}{x_i}} \quad (1.5)$$

b. Dispersion indices – which provide information about the scattering degree of individual values around the central value.

b.1 The variation range defined as:

$$A = x_{\max} - x_{\min} \quad (1.6)$$

b.2 The mean deviation or the average of residuals, defined as the sum of all residuals divided by n :

$$\bar{d}_m = \frac{\sum (x_i - \bar{x})}{n} \quad (1.7)$$

The average of residuals is always zero. This means that the average is not very useful as a characterization of the scattering degree.

b.3 The mean *absolute* deviation:

$$\bar{d}_m = \frac{\sum |x_i - \bar{x}|}{n} \quad (1.7')$$

b.4 The most useful dispersion index is *the standard deviation*. In defining the standard deviation, we get around the problem of handling the negative residuals by squaring each deviation, thereby obtaining a quantity, which is always positive. We take the average of the squares and then take the square root of this result. Thus, the standard deviation can also refer to as the root-mean-square deviation, in that it is the square root of the mean of the squares of the deviations.

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}} \quad (1.8)$$

The square of the standard deviation, s^2 , is called the variance of the set of observations. Note that s always has the same units as x , is positive and refers to an individual measurement.

In defining these indices, the averaging refers to the number n for the whole population. When only a sample (selection) of this population is measured, n should be replaced by $n-1$.

For the average, x_m , the corresponding standard deviation is given by:

$$x_m = \bar{x} \pm \frac{s}{\sqrt{n}} \quad (1.8')$$

For a normal distribution of errors, when the number of measurements is larger than 50, the result for an individual measurement is required as an interval of confidence such as:

$$x = \bar{x} \pm k \cdot s \quad (1.9)$$

with: $k = 1$ when the considered range contains 66.67% of measurements;

$k = 2$ when the considered range contains 95.00% of measurements;

$k = 3$ when the considered range contains 99.70% of measurements.

We choose the k value by taking into account the magnitude of the standard deviation and the confidence interval.

A similar procedure is applied for the calculation of x_m .

When the number of measurements is lower than approximately 50, the error distribution function is more complex and is known as the Student distribution function. The variable k is then a function of both n and the confidence interval and can be calculated or taken from tables.

1.3. The propagation of errors

The propagation of errors is nothing but another way of describing the fact that if one uses various experimental observations to calculate a result, and if the observation has errors, then the result will also be in error by an amount which depends on the errors of the individual measurements.

We consider a function z which is to be calculated from two measured amounts, x and y . We also know the standard deviations s_x and s_y and the absolute errors, ϵ_x and ϵ_y , for n measurements; $z = f(x, y)$ and

$$\bar{z} \pm \epsilon_z = f(\bar{x} \pm \epsilon_x, \bar{y} \pm \epsilon_y) \quad (1.10)$$

By developing in Taylor series we obtain:

$$f(\bar{x} \pm \epsilon_x, \bar{y} \pm \epsilon_y) = f(\bar{x}, \bar{y}) + \frac{\partial z}{\partial x} \cdot \epsilon_x + \frac{\partial z}{\partial y} \cdot \epsilon_y + \dots + \text{higher terms} \quad (1.11)$$

The variance becomes equal to:

$$s_z^2 = \frac{\sum \epsilon_z^2}{n} = \frac{\left[\left(\frac{\partial z}{\partial x} \right)^2 \cdot \sum \epsilon_x^2 + \left(\frac{\partial z}{\partial y} \right)^2 \cdot \sum \epsilon_y^2 + 2 \cdot \frac{\partial z}{\partial x} \cdot \frac{\partial z}{\partial y} \overbrace{\sum \epsilon_x \cdot \sum \epsilon_y}^{=0} \right]}{n} = \quad (1.12)$$

$$= \left(\frac{\partial z}{\partial x} \right)^2 \cdot s_x^2 + \left(\frac{\partial z}{\partial y} \right)^2 \cdot s_y^2$$

The product $\sum \epsilon_x \cdot \sum \epsilon_y$ tends to be negligible if the two errors are completely random (uncorrelated).

The standard deviation is:

$$s_z = \sqrt{\left[\left(\frac{\partial z}{\partial x} \right)^2 \cdot s_x^2 + \left(\frac{\partial z}{\partial y} \right)^2 \cdot s_y^2 \right]} \quad (1.13)$$

Observations:

For addition and subtraction the standard deviation of the sum is smaller than the sum of standard deviations of each measured amount:

$$s_x = \sqrt{s_x^2 + s_y^2}$$

For multiplication and division – large errors may appear because of the additive properties of deviation.

These relations are valid only when x and y are independent amounts; otherwise, their application yields to unsuitable results.

Exercises

1. The content of oxides in 20 samples of sodium hydroxide is:

0.166	0.144	0.128	0.044	0.214	0.192	0.228	0.084	0.136	0.192
0.124	0.178	0.126	0.761	0.011	0.172	0.192	0.104	0.162	0.154

Calculate the mean of oxides content, the standard error of an individual measurement, the standard error of the mean and the 95% confidence limit for a normal distribution law.

2. The rate constant of a chemical reaction between 5°C and 85°C is:

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \quad (1.14)$$

where $A = (1.4 \pm 0.1) \times 10^9 \text{ s}^{-1}$; $E = (103 \pm 1) \text{ kJ/mol}$. Calculate the rate constant and the 95% confidence limit for a normal distribution law at 63°C, if the standard deviation in measuring the temperature is $\pm 5^\circ\text{C}$.

1.4. Graphical Analysis of the Experimental Data

This type of analysis is required in order to follow the trend of a function and to obtain information of its characteristic parameters (e. g. the intercept and the slope for a straight line).

The requests for a correct procedure are:

- Draw the dependent versus independent variable on a xOy chart;
- Always label the function and the units of measurement on the axis;
- In case that an extrapolation is not required, use the whole space by plotting only the range of interest;
- Always show only the significant divisions, not the individual values of experimental points;
- Draw a line or a curve among the experimental points.

Exercise

Draw the variation of conversion at equilibrium versus temperature using the following data:

$t, ^\circ\text{C}$	10	20	30	40	45	50	60
X, %	16.05	23.4	26.4	27.7	31.2	36.2	37.9

1.4.1. Graphical Determination of Tangents and Areas

In the case of linear dependences, the parameters of the straight line are the intercept with Oy axis and the slope.

Example

Draw a straight line, through the points, using the data from the exercise. Prolong the line until it intersects the Oy axis. That is the intercept. The slope is determined from the rectangular triangle (Fig. 1.2):

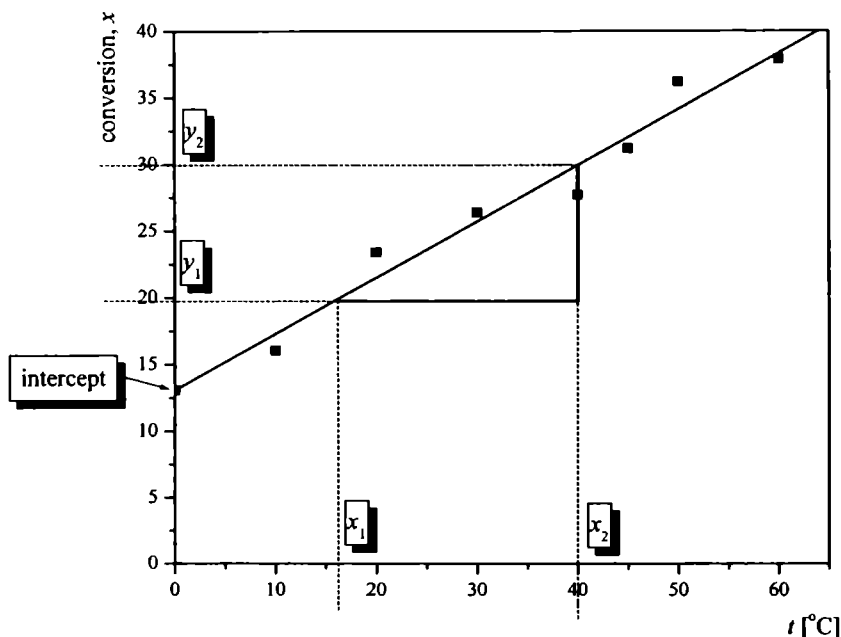


Fig. 1.2: Correct representation of $x = f(T)$; $\text{tg } \alpha = \frac{y_2 - y_1}{x_2 - x_1} = \frac{30 - 19.78}{40 - 16.28} = 0.43^\circ \text{C}^{-1}$

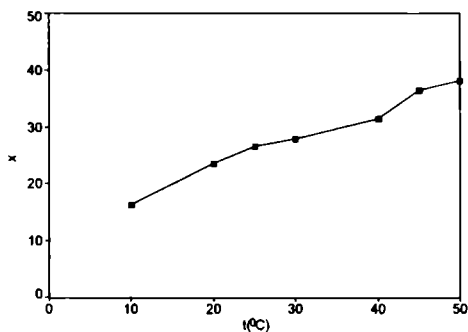
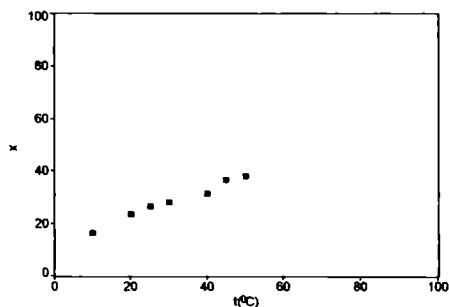


Fig. 1.3: Incorrect representations of $x = f(T)$.

When the dependence is not linear, the **method of cords** (Fig. 1.4) is used, in order to calculate the tangent. Draw a smooth curve through the points. Then place the tip of a compass in the point of interest and mark two circle arcs on the both sides of the curve. By connecting the points of each arc, results two cords. The slope of the line that connects the intersection of cords with the considered point represents a good approximation of the tangent.

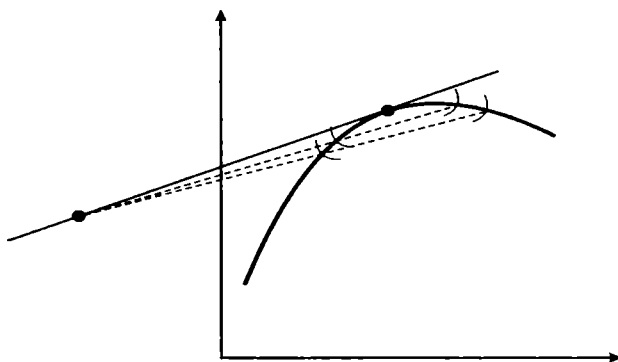


Fig. 1.4: Method of cords.

A method used in determining the areas consists in dividing the surface below in rectangles (Fig. 1.5) and measuring their areas. Another method consists in cutting the area, weighting and comparing to the mass of a sheet of known specific area. Some other more refined methods allow the calculation of such areas with better precision.

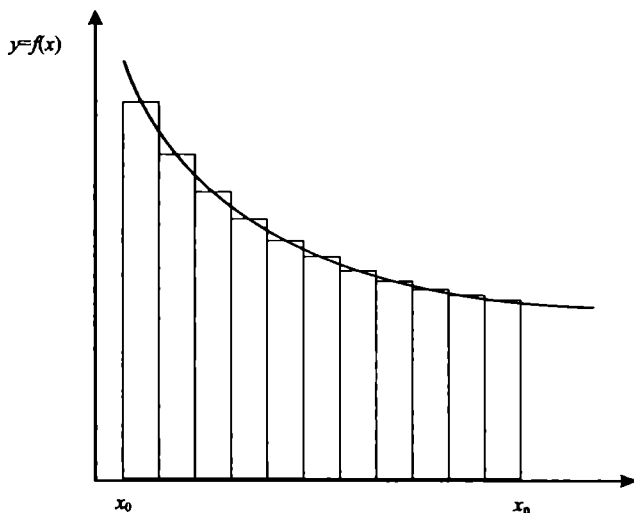


Fig. 1.5: Determination of surface area by the rectangles method

1.5. Numerical Analysis of the Experimental Data

1.5.1. Linear Models

A model can be represented quantitatively by a characteristic equation (or by a system of equations), giving a relationship between a dependent (or response) variable and one or several independent variables. The equation contains also one

or several characteristic parameters. The numerical analysis of experimental data implies the evaluation of the characteristic parameters from a set of measured values of independent and dependent variables.

The main characteristic of linear models is that the measured quantity is linearly dependent upon the parameters in the model. Beer's law is a linear model with respect to both proportionality constant and independent variable C_j . If we measure the absorbance A_j at various concentrations C_j of an absorbing chemical species, the model has the form:

$$A = b \cdot C_j \quad (1.15)$$

The only parameter in this model is b , the product of cell thickness and the molar absorptivity. In the interest of generality, we will convert A in (1.15) into a measured, response or **dependent** variable y and convert C to x , which is the experimentally controlled or **independent** variable:

$$y_j = b \cdot x_j \quad (1.16)$$

If we include the constant background signal a , the eqn.1.15 can be written in the form of a general straight line:

$$y_j = b \cdot x_j + a \quad (1.17)$$

Eqn. 1.17 is a linear model because **the independent variable y is a linear function of the model parameters, b and a** , and not because the equation describes a straight line. The model needs not to be a straight line to be linear. For example a polynomial function like:

$$y = a_0 + a_1 \cdot x + a_2 \cdot x^2 + \dots \quad (1.17')$$

is a linear function with respect to parameters a_j .

1.5.2. Linear Regression Analysis

When a model is linear it means that we can fit it into experimental data by the method of linear regression. The principles used in linear least squares method also apply to nonlinear regression analysis.

In order to discuss this principle, we express a single-equation linear model with k parameters and a single independent variable x_j , in the general form:

$$y_{j(\text{calc})} = f(x_j, a_1, a_2, \dots, a_k) \quad (1.18)$$

where $y_{j(\text{calc})}$ depends linearly on the parameters $a_1, a_2, \dots, a_k$. Eqn.1.18 provides a way to compute the response $y_{j(\text{calc})}$ from the linear model.

We also have n experimental measured $y_{j(\text{meas})}$ one at each x_j . For a set of n measured values $y_{j(\text{meas})}$, we define the error sum:

$$S = \sum_{j=1}^n w_j \cdot \left[y_{j(\text{meas})} - y_{j(\text{calc})} \right]^2 \quad (1.19)$$

where w_j are weighting factors that depend on the distribution of random errors in y . The simplest set of assumptions is as it follows: the x values are free of errors and the random errors in y are independent of the magnitude of the $y_{j(\text{meas})}$. Another way of expressing this error distribution is that the variances in all of the y_j (s_y^2 , where s_y is the standard deviation in y) are equal (i.e. w_j is constant).

The principle of least squares is used in both linear and nonlinear regression. Its major premise is that the best values of the parameters $a_1, \dots, a_k$ will be obtained when the error sum is at a minimum value with respect to these parameters. Exact formulas for the parameters can be derived for a linear model by taking the first derivative of S with respect to each parameter and setting each of these derivatives equal to zero. This results in a set of linear simultaneous equations that can be solved in closed form for the unique value of each parameter.

1.5.2.1. Linear regression on a straight-line

Consider this procedure to the straight-line model in (1.17), where the form of error sum is:

$$S = \sum_{j=1}^n \left[y_{j(\text{meas})} - b \cdot x_j - a \right]^2 = \sum_{j=1}^n \epsilon_j^2 \quad (1.20)$$

For a given set of data, S depends on parameters b and a . The required derivatives are:

$$\begin{cases} \frac{\partial S}{\partial a} = 0 \\ \frac{\partial S}{\partial b} = 0 \end{cases} \quad (1.21)$$

Eqn. 1.21 yields a system of two equations with two unknowns, a and b , respectively:

$$\begin{cases} n \cdot a + b \cdot \sum_{j=1}^n x_j = \sum_{j=1}^n y_j \\ a \cdot \sum_{j=1}^n x_j + b \cdot \sum_{j=1}^n x_j^2 = \sum_{j=1}^n x_j \cdot y_j \end{cases} \quad (1.22)$$

Solving this system one obtains the slope and the intercept:

$$b = \frac{n \cdot \sum x_j \cdot y_j - \sum x_j \cdot \sum y_j}{n \cdot \sum x_j^2 - (\sum x_j)^2} \quad (1.23)$$

$$a = \frac{\sum x_j^2 \sum y_j - \sum x_j \cdot y_j \cdot \sum x_j}{n \cdot \sum x_j^2 - (\sum x_j)^2} \quad (1.24)$$

An important question to be answered as a part of any regression analysis is: how well does the model fit the data, or what is the goodness of fit? The correlation coefficient is a statistic often used to test goodness of fit of linear least squares models to data. This correlation coefficient (r) is defined as:

$$r = \frac{n \cdot \sum x_j \cdot y_j - \sum x_j \sum y_j}{\sqrt{[n \cdot \sum x_j^2 - (\sum x_j)^2] \cdot [n \cdot \sum y_j^2 - (\sum y_j)^2]}} \quad (1.25)$$

and has values from -1 to $+1$. A value of $r = +1$ demonstrates a perfect correlation between x and y and similarly for $r = -1$, when the slope is negative. Lower absolute values, approaching zero indicate poorer and poorer correlations. Nevertheless it is difficult to choose the value for which a result may be accepted. Advanced statistical analysis gives objective criteria for such a choice. An alternative way to characterize the goodness of fit is to calculate the standard deviations in each parameter (s_a and s_b):

$$s_b^2 = \sum_{j=1}^n \left(\frac{\partial b}{\partial y_j} \right)^2 \cdot s_y^2 = \frac{n^2}{n \cdot \sum x_j^2 - (\sum x_j)^2} \cdot s_y^2 \quad (1.26)$$

$$s_a^2 = \sum_{j=1}^n \left(\frac{\partial a}{\partial y_j} \right)^2 \cdot s_y^2 = \frac{\sum x_j^2}{n \cdot \sum x_j^2 - (\sum x_j)^2} \cdot s_y^2$$

where $s_y^2 = \frac{S}{n-2}$

We may decide whether or not a model is suitable according to s_a and s_b values.

Example. Applying the least squares method to the following kinetic data:

$t, ^\circ\text{C}$	10	20	30	40	45	50	60
X, %	16.05	23.4	26.4	27.7	31.2	36.2	37.9

we obtain:

$\sum x_j$	$\sum x_j^2$	$\sum y_j$	$\sum y_j^2$	$\sum x_j \cdot y_j$
255	11125	198.85	5989.7025	8016.5

and:

$$a = \frac{11125 \cdot 198.85 - 255 \cdot 8016.5}{7 \cdot 11125 - (255)^2} = \frac{167998.75}{12850} = 13.074$$

$$b = \frac{7 \cdot 8016.5 - 255 \cdot 198.85}{7 \cdot 11125 - (255)^2} = \frac{5408.75}{12850} = 0.4209$$

$$r = \frac{5408.75}{\sqrt{(12850) \cdot (7 \cdot 5989.7025 - 198.85^2)}} = \frac{5408.75}{5537.8466} = 0.9766$$

$$s_b = \sqrt{\frac{49}{12850} \cdot (1.715)^2} = 0.1058$$

$$s_a = \sqrt{\frac{11125}{12850} \cdot (1.715)^2} = \sqrt{0.8657} = 1.60$$

The result is: $\begin{cases} a = 13.07 \pm 1.60\% \\ b = 0.4209 \pm 0.1058 \text{ } ^\circ\text{C}^{-1} \end{cases}$

1.5.2.2. Multiple linear regressions

When the dependence of measured amount y_j on more x_j variables takes the form:

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + \dots + a_p \cdot x_p \quad (1.27)$$

we may calculate the a_j parameters assuming that the error sum is at a minimum value with respect to these parameters. The independent variables x_j are free of errors and the variances in all of the y_j (s_y^2 , where s_y is the standard deviation in y) are equal. The error sum is:

$$S = \sum_{j=1}^n (y_j - a_0 - a_1 \cdot x_{j1} - a_2 \cdot x_{j2} - \dots - a_p \cdot x_{jp})^2 \quad (1.28)$$

From the minimization conditions results:

$$\begin{cases} \frac{\partial S}{\partial a_0} = 0 \\ \frac{\partial S}{\partial a_1} = 0 \\ \vdots \\ \frac{\partial S}{\partial a_p} = 0 \end{cases} \quad (1.29)$$

System (1.29) yields p equations with p unknowns. The system can be solved using numerical methods such as Gauss – Jordan and matrix inversion methods. The

advantage of using multiple linear regressions is reducing the experimental time and working simultaneously in different conditions (changing all independent variables).

1.5.2.3. Polynomial regression

This method consists in fitting a polynomial function such as:

$$y = a_0 + a_1 \cdot x + a_2 \cdot x^2 + \dots + a_p \cdot x^p \quad (1.30)$$

on experimental data. Assuming that $x_1 = x$, $x_2 = x^2$, ..., $x_p = x^p$, the a_p parameters can be estimated applying the previously described multiple linear regression.

The polynomial regression is often used in chemical kinetics, especially in calculating the instant rates. Generally, the kinetic data are obtained as (t, C_j) pairs. The reaction rate can be determined using either a graphical procedure (in this case the result is affected by large errors), or by fitting a polynomial function on the experimental data $C = f(t)$. The appropriate function is chosen for the best value of the correlation coefficient r .

If C is the dependent variable and t is the independent one, then (1.30) becomes:

$$C = a_0 + a_1 \cdot t + a_2 \cdot t^2 + \dots + a_p \cdot t^p \quad (1.31)$$

The instant reaction rate can be easily calculated from the first derivative of this function with respect to time:

$$v_r = \frac{1}{\nu} \cdot \frac{dC}{dt} = \frac{1}{\nu} \cdot (a_1 + 2 \cdot a_2 \cdot t + 3 \cdot a_3 \cdot t^2 + \dots + p \cdot a_p \cdot t^{p-1}) \quad (1.32)$$

where ν is the stoichiometric coefficient of chosen component.

1.5.3. Nonlinear Models

Single equation nonlinear models are those in which the dependent variable y depends in a nonlinear fashion on at least one of the parameters in the model. Example:

First-order decay:
$$y = a \cdot \exp(-b \cdot x) \quad (1.33)$$

1.5.3.1. Nonlinear regression

As in linear regression, the goal of nonlinear regression is to find the absolute minimum in the error sum with respect to all parameters. If we calculate S in (1.19) for a nonlinear model and set the first derivative with respect to each parameter equal to zero, we will find that the set of simultaneous equation does not yield closed form solutions. The alternative is to find the minimum S by numerical

methods, using a **minimization algorithm** representing a sequence of repetitive mathematical operations.

Computer programs for nonlinear regression analysis begin from a set of best guesses for the parameters in the model, as provided by the user. The minimization algorithm varies the parameters in a repetitive series of successive computational cycles, which are the steps leading toward the minimum S . At the end of each cycle, a new, and presumably smaller, value of S is computed from the new set of parameters found by the algorithm. These cycles are called iterations.

The Gauss-Newton algorithm, frequently used in minimization algorithms, approximates nonlinear models for $y_{j(\text{calc})}$ by linear Taylor series expansions. After initial guesses new values of parameters are found at each cycle, using expressions involving first derivatives of S with respect to each parameter. Ideally, each iterative cycle gives successively better estimates for the parameters until the absolute minimum in S is reached.

1.5.4. Exercises

1. The temporal dependence of a reactant concentration is shown in the following table:

t, s	15	30	60	90	120	150	180	210	240
C, M	0.053	0.043	0.027	0.019	0.014	0.011	0.007	0.005	0.003

Calculate (using the graphical procedure) the instant reaction rates at $t = 60 \text{ s}$ and $t = 180 \text{ s}$.

2. Plot the calibration straight line for the photometric determination of benzene in alcoholic solution, using the absorbance-concentration data:

$C(\text{g/l})$	0.2	0.5	1.0	1.5	2.0	2.5	3
A	0.20	0.37	0.64	0.93	1.22	1.50	1.80

Compare the results to those obtained using the least squares method. What is the standard deviation in each parameter of the straight line?

3. The polynomial function:

$$C = 0.067 - 1.05 \cdot 10^{-3} \cdot t + 8.15 \cdot 10^{-6} \cdot t^2 - 3.13 \cdot 10^{-8} \cdot t^3 + 4.57 \cdot 10^{-11} \cdot t^4$$

was fitted on the experimental data from ex. 1. Calculate the instant reaction rates at $t = 60 \text{ s}$ and $t = 180 \text{ s}$. Compare the result to those obtained at ex. 1.

Part I: Practical Works

2. Determination of the Viscosity of Fluid Media

2.1. Theoretical Background

The viscosity represents the resistance of the fluids against flow. If one considers the fluid consisting of parallel layers, the friction force between two consecutive layers, having a dx separation distance, which undergo parallel movement with a relative velocity v , is proportional to the velocity gradient (Newton's Law):

$$F = -\eta \cdot \frac{dv}{dx} \cdot S \quad (2.1)$$

where η is the viscosity of the fluid. Unit of measurement is $N \times m^{-2} \times s$ or $kg \times m^{-1} \times s^{-1}$. Another accepted unit in older CGS system is the Poise $1 \text{ Poise} = g \times cm^{-1} \times s^{-1}$, $1 N \times m^{-2} \times s^{-1} = 10 \text{ Poise}$.

The liquids having simple structure – newtonian liquids – obey the Newton's Law, the viscosity being independent on the velocity gradient. There are also liquids that override eqn. (2.1); these are so-called non-newtonian liquids and, generally speaking, they are solutions of substances bearing more complex or even macromolecular structure. The viscosity depends on the size of the molecules and also on the forces of interaction between them.

The dissolution of either non-ionic, ionic, micromolecular or macromolecular compounds modifies the viscosity of the solution.

The non-electrolytes change the solvent viscosity even in dilute solutions, due to specific interactions between the molecules of the non-electrolyte and of the solvent. In the case of alcohol solutions in water a maximum value for the viscosity appears at a certain concentration, depending on the nature of the alcohol.

In the case of ideal mixtures of liquids, the viscosity depends on the components molar fraction. The viscosity of aqueous solutions of electrolytes depends on the properties of the ions – size and charge; in the range of dilute solutions – $0.002 \div 0.1 \text{ M}$ – it shows a linear dependence on the concentration.

The most common methods for the determination of the viscosity of liquids rely on the examination of the flow through a capillary tube. The volume of the liquid, V , leaking through a capillary, driven by the pressure p , within the time t , is a function of the capillary radius r , the tube length l and the viscosity of the liquid (Poiseuille's relation):

$$V = \frac{\pi \cdot r^4 \cdot p \cdot t}{8 \cdot \eta \cdot l} \quad (2.2)$$

2.2. Experimental Method

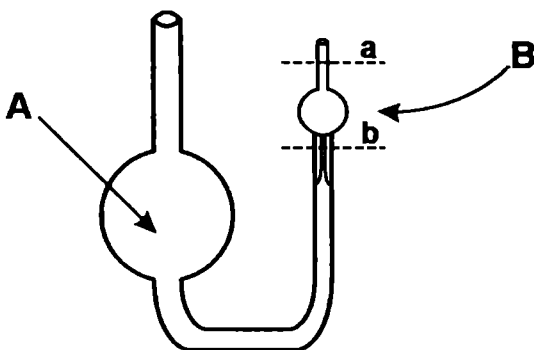


Fig. 2.1: Ostwald viscometer.

The Ostwald viscometer (see Fig. 2.1) can be used only for the determination of viscosity in the case of the liquids with small and average viscosity. Two flasks, A and B, connected by an U-shaped glass tube provided with a capillary zone disposed below the B flask, compose the viscometer.

The A flask is filled with the test liquid, then the liquid is raised through the capillary tube until it reaches a level above the mark **a**. Then the liquid is allowed to freely leak from the B flask, through the capillary tube, recording the time necessary for it to pass from the **a** level to the **b** level. Thus the viscosity of any liquid can be determined, relative to a reference liquid whose viscosity is known.

Applying the Poiseuille's relation to the reference liquid, whose viscosity and density are η_0 and ρ_0 , respectively, one obtains:

$$V = \frac{\pi \cdot r^4 \cdot p \cdot t_0}{8 \cdot \eta_0 \cdot l} \quad (2.3)$$

and knowing that the pressure p is the pressure of the liquid column:

$$p = h \cdot g \cdot \rho_0 \quad (2.4)$$

results:

$$V = \frac{\pi \cdot r^4 \cdot h \cdot g \cdot \rho_0 \cdot t_0}{8 \cdot \eta_0 \cdot l} \quad (2.5)$$

The same procedure is applied to the liquid under investigation, whose viscosity and density are η_X and ρ_X , respectively:

$$V = \frac{\pi \cdot r^4 \cdot h \cdot g \cdot \rho_X \cdot t_X}{8 \cdot \eta_X \cdot l} \quad (2.6)$$

The unknown viscosity, η_X , can be measured from the ratio between (2.5) and (2.6):

$$\eta_X = \eta_0 \frac{\rho_X \cdot t_X}{\rho_0 \cdot t_0} \quad (2.7)$$

2.3. Determination of Viscosity of Methanol-Water Mixtures

The aim of the present experimental part is investigation of viscosity dependence on concentration, for several mixtures of methyl alcohol and water. For each mixture and pure component, 5 runs will be made, recording the time necessary for liquid to flow between a and b levels marked on the viscometer.

Knowing that the alcohol density dependence on alcohol concentration (% vol) in water is:

$$\rho_X = 0.996 - 1.57 \cdot 10^{-3} \cdot c + 9.88 \cdot 10^{-6} \cdot c^2 - 1.24 \cdot 10^{-7} \cdot c^3 \left(\frac{\text{kg}}{\text{dm}^3} \right) \quad (2.8)$$

one can calculate the viscosity by applying (2.7), using water as the reference liquid, for which $\rho_0 = 0.996 \frac{\text{kg}}{\text{dm}^3}$ and $\eta_0 = 1 \text{cPoise}$ (centipoises).

The experimental data will be drawn on a millimetre sheet, as $\eta = f(c)$, and observations concerning viscosity behaviour will be made upon visual inspection of the graph.

3. Determination of Activation Energy of Viscous Flow

3.1. Theoretical Background

The viscosity represents the resistance of the fluids against flow; it depends on the fluid behaviour to flow – newtonian and non-newtonian liquids – and also on the fluid structure. The viscosity of the fluids shows an exponential dependence on the temperature:

$$\eta = B \cdot e^{\frac{E_v}{R \cdot T}} \quad (3.1)$$

where E_v is the activation energy of the process of viscous flow, in $\text{J} \times \text{mol}^{-1}$, B is the pre-exponential factor, T is the absolute temperature, in K, and R is the gas constant, in $\text{J} \times \text{mol}^{-1} \times \text{K}^{-1}$.

The activation energy of the process of viscous flow is related to other physical properties of the fluid, like the heat of vaporisation, H_{vap} , as follows:

$$E_v = \frac{H_{\text{vap}}}{n} \quad (3.2)$$

where n is a constant responsible for the liquid structure, and it takes values within the range of 1 to 4.

The logarithmic form of (3.1) allows the graphical measurement of the activation energy, from the slope of the linear dependence:

$$\ln \eta = f\left(\frac{1}{T}\right) = \ln B + \frac{E_v}{R} \cdot \frac{1}{T} \quad (3.3)$$

For high viscous liquids, the determination of the viscosity can be performed by the **method of falling body**, recording the time necessary for a solid body to freely fall between two marks in a viscous environment – the test liquid.

Despite the fact that the fall of the bodies in vacuum is an uniformly accelerating movement, for viscous media, the movement is slowed by the friction force, whose

main effect is the establishment of an equilibrium between the apparent body weight, G_{app} , and the friction force, F_f :

$$G_{app} = F_f \quad (3.4)$$

On the other hand, G_{app} can be expressed by the difference between the actual body weight, G , and the Archimedes's Force (the weight of the dislocated volume), F_A :

$$G_{app} = G - F_A = V \cdot g \cdot \rho_s - V \cdot g \cdot \rho_l = V \cdot g \cdot (\rho_s - \rho_l) \quad (3.5)$$

where V is the volume of the solid body, g is the gravitational acceleration, ρ_s and ρ_l are the density of the solid and liquid, respectively.

For laminar flow F_f is a function of the fall velocity of the solid body, v , and of the liquid viscosity, η :

$$F_f = k \cdot v \cdot \eta \quad (3.6)$$

where k is a constant taking into account the geometry of the solid body.

For a sphere (solid ball) of a known radius, r , one obtains:

$$\frac{4\pi r^3}{3} \cdot g \cdot (\rho_s - \rho_l) = 6\pi \cdot r \cdot v \cdot \eta \quad (3.7)$$

which can be further expressed as:

$$\eta = \frac{2}{9} \cdot g \cdot r^2 \cdot \frac{(\rho_s - \rho_l)}{v} \quad (3.8)$$

Because the ball movement in a viscous environment is uniform, its velocity, v , can be obtained by measuring the time, t , necessary for the ball to fall a distance of a known length, s , so that:

$$v = \frac{s}{t} \quad (3.9)$$

Equations (3.8) and (3.9) allow expressing the viscosity of the liquid as:

$$\eta = K \cdot (\rho_s - \rho_l) \cdot t \quad (3.10)$$

3.2. Experimental Part

The experiments will be performed with a Hoppler viscometer, consisting of a double-walled glass tube connected to a thermostat, filled with the test liquid – glycerine – and provided with a stainless steel sphere. The tube is twice marked allowing the measurement of the time necessary for the ball to fall between them.

The activation energy of the viscous flow process can be evaluated by measuring the viscosity of the glycerine at several temperatures (at least five) within the range 20÷60°C; three runs will be performed for each selected temperature, and the average time will be recorded. The acquired data will be further used to compute the viscosities, according to (3.10), and knowing that:

$$K = 1,65 \text{ Poise} \left(\frac{\text{s} \cdot \text{kg}}{\text{dm}^3} \right); \rho_s = 8,11 \frac{\text{kg}}{\text{dm}^3}$$

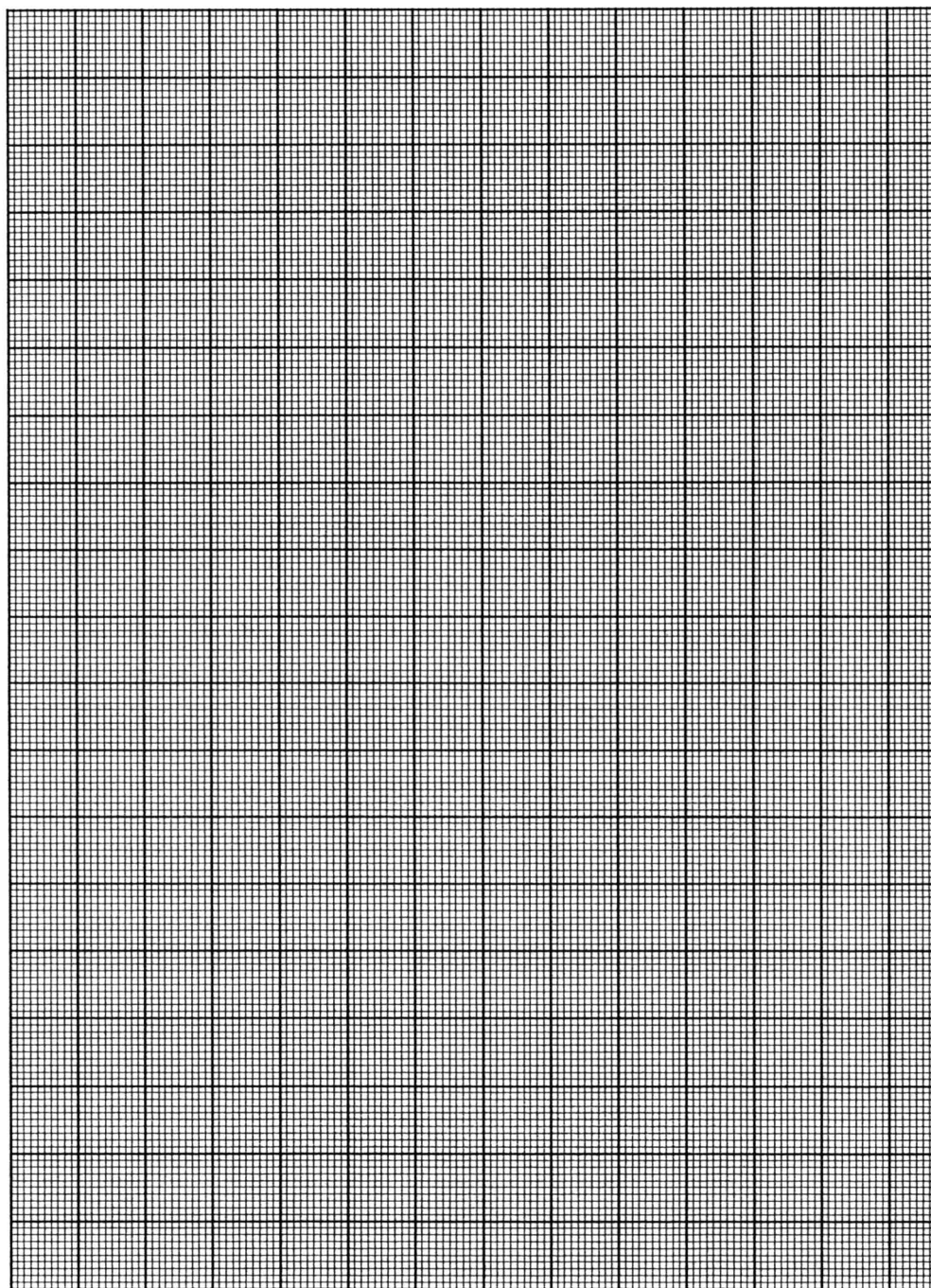
and that the glycerine density depends on the temperature (in °C), as follows:

$$\rho_{\text{glycerine}} = 1.282 - 1.51 \cdot 10^{-3} \cdot t + 2.71 \cdot 10^{-5} \cdot t^2 - 1.85 \cdot 10^{-7} \cdot t^3$$

The slope of the plot $\ln \eta = f\left(\frac{1}{T}\right)$ allows the evaluation of the activation energy of the viscous flow process.

3.3. Experimental Data Report

No.	T (K)	Time (s)	$\bar{t}$	$\rho_{\text{glycerine}}$ $\left(\frac{\text{kg}}{\text{dm}^3}\right)$	η (P)	$\ln \eta$	$1/T$
1							
2							
3							
4							
5							



4. Determination of Surface Tension of Liquids

4.1. Theoretical Background

The particles within an interface undergo different interactions with the particles belonging to the two phases. For a gas–liquid system gas molecules exhibit attractive forces much weaker than the molecules from the inner liquid, so that molecules from the surface layer are driven through the inner liquid by a non-equilibrated attractive force, having a normal direction to the liquid surface, which tends to lower the liquid surface. The tangential force to the liquid surface is called **the surface tension**, and represents the force that acts at the liquid-gas interface; the international units are $\text{N} \times \text{m}^{-1}$, and in CGS system are $\text{dyne} \times \text{cm}^{-1}$.

The presence of foreign dissolved molecules in the liquid phase can modify the surface tension of the liquid due to their specific interaction with the molecules of the surface layer.

Both static and dynamic methods can be used for the determination of surface tension. Among the static methods one can mention the method based on capillary ascension of a liquid; an example of a dynamic method is based on the stalagmometer.

4.2. Experimental Part

The surface tension of aqueous solutions of acetic acid will be determined by using the stalagmometer method. The basic principle consists in the establishment of equilibrium between the weight of a droplet formed upon the slow flow of a liquid through a capillary, and the force of surface tension:

$$m \cdot g = 2 \cdot \pi \cdot r \cdot \gamma \quad (4.1)$$

where m is the mass of the droplet, g is the gravitational acceleration, r is the capillary radius, and γ is the surface tension.

If one records the number of fallen droplets, n , corresponding to a known volume of liquid, V , whose mass and density are M and ρ , respectively, the weight of a droplet is then $M \cdot g/n$ or $V \cdot \rho \cdot g/n$. Eqn (4.1) becomes:

$$\frac{V \cdot \rho \cdot g}{n} = 2 \cdot \pi \cdot r \cdot \gamma \quad (4.2)$$

The capillary radius can be eliminated by the help of a reference liquid, whose surface tension is known – water for instance:

$$\frac{V \cdot \rho \cdot g_0}{n_0} = 2 \cdot \pi \cdot r \cdot \gamma_0 \quad (4.3)$$

where “ $_0$ ” designates the reference condition.

The comparison between eqns (4.2) and (4.3) allows obtaining a simple expression for the determination of the surface tension of the test liquid, γ_X :

$$\gamma_X = \gamma_0 \cdot \frac{\rho_X}{\rho_0} \cdot \frac{n_0}{n_X} \quad (4.4)$$

4.3. Determination of the Surface Tension of Water – Acetic Acid Mixtures

The experimental stalagmometer is shown in Fig. 4.1. The droplets corresponding to the volume **ab**, leak through the orifice marked **c**. The numbers of droplets, n and n_0 , will be recorded and, by applying (4.4), the surface tension will be calculated. Distilled water will be used as reference liquid, whose surface tension and density are $\gamma_0 = 72.15 \cdot 10^{-3} \text{ N} \cdot \text{m}^{-1}$ and $\rho_0 = 0.998 \text{ kg} \times \text{dm}^{-3}$, respectively.

The surface tension for the following concentrations of acetic acid in water will be determined:

- 5% ($\rho_{5\%} = 1.0035 \text{ kg} \times \text{dm}^{-3}$)
- 10% ($\rho_{10\%} = 1.0126 \text{ kg} \times \text{dm}^{-3}$)
- 15% ($\rho_{15\%} = 1.0195 \text{ kg} \times \text{dm}^{-3}$)
- 20% ($\rho_{20\%} = 1.0261 \text{ kg} \times \text{dm}^{-3}$)
- 40% ($\rho_{40\%} = 1.0453 \text{ kg} \times \text{dm}^{-3}$)

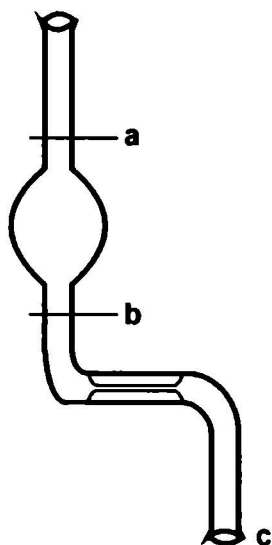
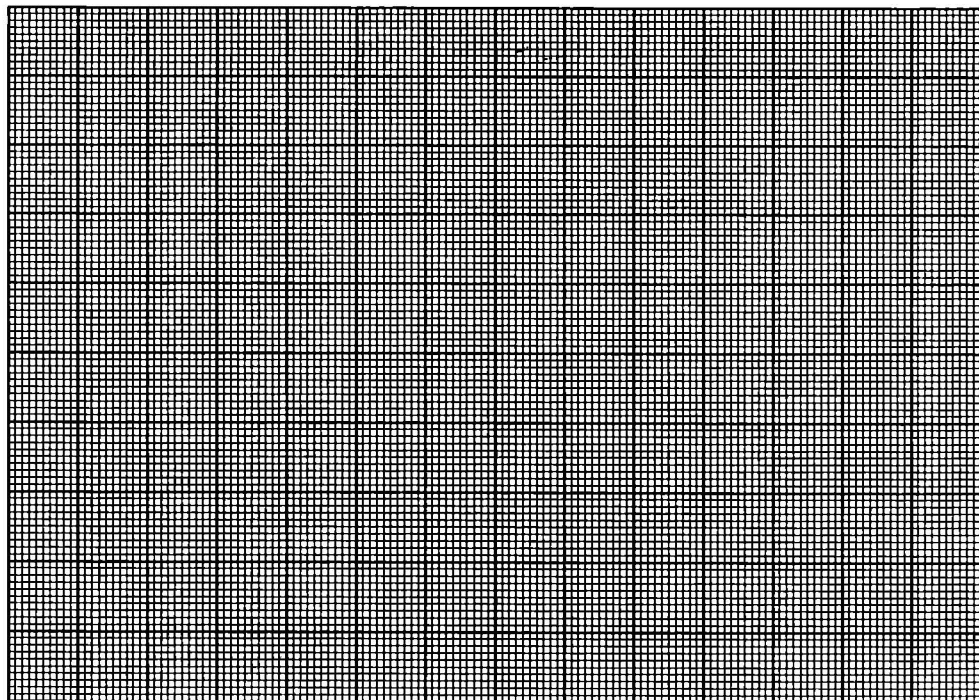


Fig. 4.1: The Stalagmometer.

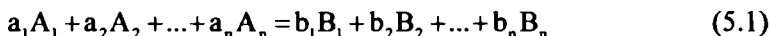
The experimental data will be drawn as $\gamma = f(c)$, and the surface tension behaviour will be rationalised.



5. Determination of the Activation Energy and Reaction Order

5.1. Theoretical Background

For a homogeneous system of volume V , where a chemical reaction occurs, represented by the following stoichiometric equation:



the **rate of transformation** relative to a certain component, i , can be expressed as follows:

$$r_i = \frac{1}{V} \cdot \frac{dn_i}{dt} \quad (5.2)$$

where n_i is the number of moles of component i , in moles, and t is time, in seconds. If reaction takes place at constant volume, and taking into account the definition of

the molar concentration, $C_i = \frac{n_i}{V}$, (5.2) becomes:

$$r_i = \frac{dC_i}{dt} \quad (5.3)$$

For a reactant r_i has negative values (n_i decreases in time) and for a product r_i has positive values (n_i increases in time).

If the stoichiometric eqn. (5.1) is written in the general form:

$$\sum_i \nu_i \cdot A_i \quad (5.4)$$

with the sign convention $\nu_i < 0$ for reactants and $\nu_i > 0$ for products, then the **reaction rate**, r_R , irrespective to the component, is given by:

$$r_R = \frac{1}{\nu_i} \cdot \frac{1}{V} \cdot \frac{dn_i}{dt} \quad (5.5)$$

or

$$r_R = \frac{1}{\nu_i} \cdot \frac{dC_i}{dt} \quad (5.6)$$

The reaction rate r_R has always positive values.

The reaction rate depends on the component concentrations and temperature, according to a **kinetic equation** of the form: $r_R = f(C_j, T)$. The actual form of the function $f(C_j, T)$ is specific to the nature of the reaction. It was found that for a great number of chemical reactions the function $f(C_j, T)$ can be factorised, i.e. it can be expressed as a product between a concentration-dependent and a temperature-dependent function:

$$f(C_j, T) = F(T) \cdot f(C_j) \quad (5.7)$$

The function $F(T)$, usually denoted by k , is called the rate constant, and the function $f(C_j)$ is a product of power functions:

$$f(C_j) = C_A^{\alpha_1} \cdot C_B^{\alpha_2} \cdot \dots \cdot C_j^{\alpha_j} \quad (5.8)$$

whose exponents α_1, α_j are the partial reaction orders.

Taking into account eqns. (5.7) and (5.8), the kinetic equation can be written as:

$$r_R = k \cdot C_A^{\alpha_1} \cdot C_B^{\alpha_2} \cdot \dots \cdot C_j^{\alpha_j} \quad (5.9)$$

The sum of the partial reaction orders gives the overall reaction order, α :

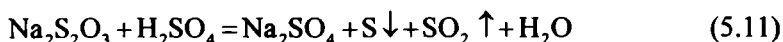
$$\alpha = \sum_j \alpha_j \quad (5.10)$$

The partial reaction orders can be measured from the reaction rate dependence on the initial concentration of the reactants, and can take positive or negative values, including zero. A simple method for determination of partial reaction order is to keep all reactant concentrations constant (in large excess) except one, and to measure its reaction order. For elementary reactions, the partial reaction order equals the stoichiometric coefficient.

The activation energy is measured from the temperature dependence of the rate constant k .

5.2. Determination of the Reaction Order

The experiment consists in investigation of the chemical reaction between sodium tiosulphate and sulphuric acid, in aqueous solution:



for which (5.9) takes the following form:

$$r_R = k \cdot C_{\text{Na}_2\text{S}_2\text{O}_3}^{\alpha_1} \cdot C_{\text{H}_2\text{SO}_4}^{\alpha_2} \quad (5.12)$$

The reaction is easy to follow because the formation of colloidal sulphur produces opalescence in the reaction vessel. The reaction rate, relative to sulphur, is

$r_R = \frac{dC_S}{dt} \cong \frac{\Delta C_S}{\Delta t}$. The quantity ΔC_S is constant, irrespective to the reactant concentration, and represents the quantity of sulphur per unit volume necessary for the colloidal precipitate to appear.

One studies the influence of sodium tiosulphate concentration on the reaction rate, and determines its partial reaction order. Keeping constant the environment temperature and the sulphuric acid concentration will result in an inverse proportionality between reaction rate and time. This is valid for the interval between the initial time, t_0 , and the time corresponding to colloidal sulphur appearance, t_5 , when practically an insignificant amount of reactants is consumed, and the reaction rate depends on the initial concentration of the sodium tiosulphate.

5.2.1. Working Procedure

Table 5.1 shows the volumes of solutions that will be added to test tubes; for the first four test tubes – mixtures of sodium tiosulphate and water to obtain 5 ml total volume, and for the last ones – 5 ml H_2SO_4 each.

Table 5.1

No.	$V_{\text{Na}_2\text{S}_2\text{O}_3}$, ml	$V_{\text{H}_2\text{O}}$, ml
1	5	0
2	4	1
3	3	2
4	2	3
5-8	0	5 ml H_2SO_4

The test tube couples 1-5 to 4-8 will be successively combined and thoroughly mixed, and the time necessary for opalescence appearance will be recorded for each couple.

5.2.2. Calculations

The relative concentration of sodium tiosulphate is calculated using the following relation:

$$C_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{V_{\text{Na}_2\text{S}_2\text{O}_3}}{V_{\text{Na}_2\text{S}_2\text{O}_3} + V_{\text{H}_2\text{O}} + V_{\text{H}_2\text{SO}_4}} \quad (5.13)$$

The slope of the linear dependence $\ln\left(\frac{1}{\Delta t}\right) = f(\ln C_{\text{Na}_2\text{S}_2\text{O}_3})$ allows determining the partial reaction order relative to $\text{Na}_2\text{S}_2\text{O}_3$, α_1 .

A comparative analysis using linear regression will be performed, and conclusion upon method reliability will be drawn.

5.3. Determination of the Activation Energy

One studies the temperature dependence of rate constant. According to Arrhenius, this dependence is given by:

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}} \quad (5.14)$$

where A is the pre-exponential factor, E_a is the activation energy, T is the absolute temperature and R is gas law constant ($R = 8.31 \text{ J} \cdot \text{mol}^{-1} \times \text{K}^{-1} \cong 2 \text{ cal} \times \text{mol}^{-1} \times \text{K}^{-1}$).

The activation energy can be calculated from the slope of the linear dependence

$$\ln\left(\frac{1}{\Delta t}\right) = f\left(\frac{1}{T}\right).$$

5.3.1. Working Procedure

Take four test tubes and pour 5 ml of $\text{Na}_2\text{S}_2\text{O}_3$ in each of it. Another four test tubes will be filled with 5 ml H_2SO_4 each. The test tubes will then be inserted in a Berzelius flask half-filled with water, and provided with a thermometer. Adjust the flask in a water-bath and record the ambient temperature. Then proceed mixing the first couple test tubes (1,5) and record the time necessary for sulphur appearance. Plug-in the water bath and raise the temperature to the nearest value within the range $30\div 60^\circ\text{C}$. Allow the attainment of equilibrium temperature, record the temperature and repeat the experiment with the next couple of test tubes (2,6).

The experiment will end when all 4 temperatures and corresponding reaction times are recorded. The results will be reported in Table 5.2.

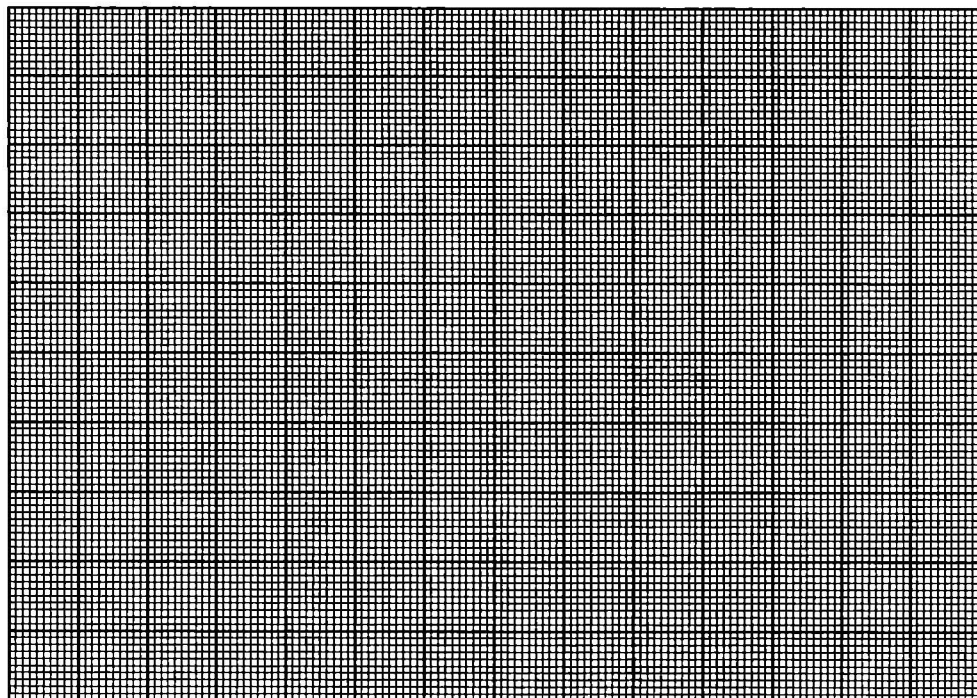
Table 5.2

No.	T, K	$\Delta t, s$	$r_R = 1/\Delta t, s^{-1}$	$\ln r_R$	$1/T \times 10^3, K^{-1}$
1					
2					
3					
4					

5.3.2. Calculations

The slope, E_a/R , of the linear dependence $\ln\left(\frac{1}{\Delta t}\right) = f\left(\frac{1}{T}\right)$ allows determining the activation energy, in joules or calories per mole.

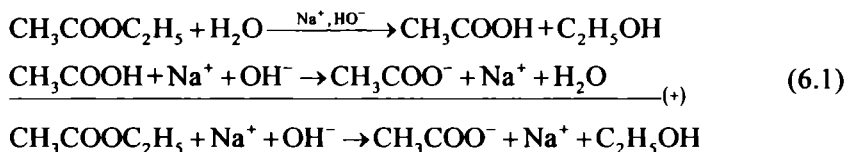
The result will be compared to that of linear regression and conclusion upon method reliability will be drawn.



6. Hydrolysis of Esters in Basic Medium. Conductometric Method

6.1. Theoretical Background

The process of base-catalysed hydrolysis of esters is an irreversible one because the resulted acid progressively neutralises the catalyst. For hydrolysis of ethyl acetate, the following stoichiometric equations are valid:



The kinetics was found to be first order relative to both ester and catalyst (HO^-). For equal concentrations of the reactants, the second order rate constant, k_2 , is:

$$k_2 = \frac{1}{a \cdot t} \cdot \frac{x}{a - x} \quad (6.2)$$

where a is the initial concentration, and x is the diminution of concentration at time t (volume reaction extent).

Because ions with different mobility are involved in reaction, the reaction rate can be easily evaluated upon measuring the temporal variation of the conductance, G , of the reaction mixture. The kinetic equation can be expressed as:

$$k_2 = \frac{1}{a \cdot t} \cdot \frac{G_0 - G_t}{G_t - G_x} \quad (6.3)$$

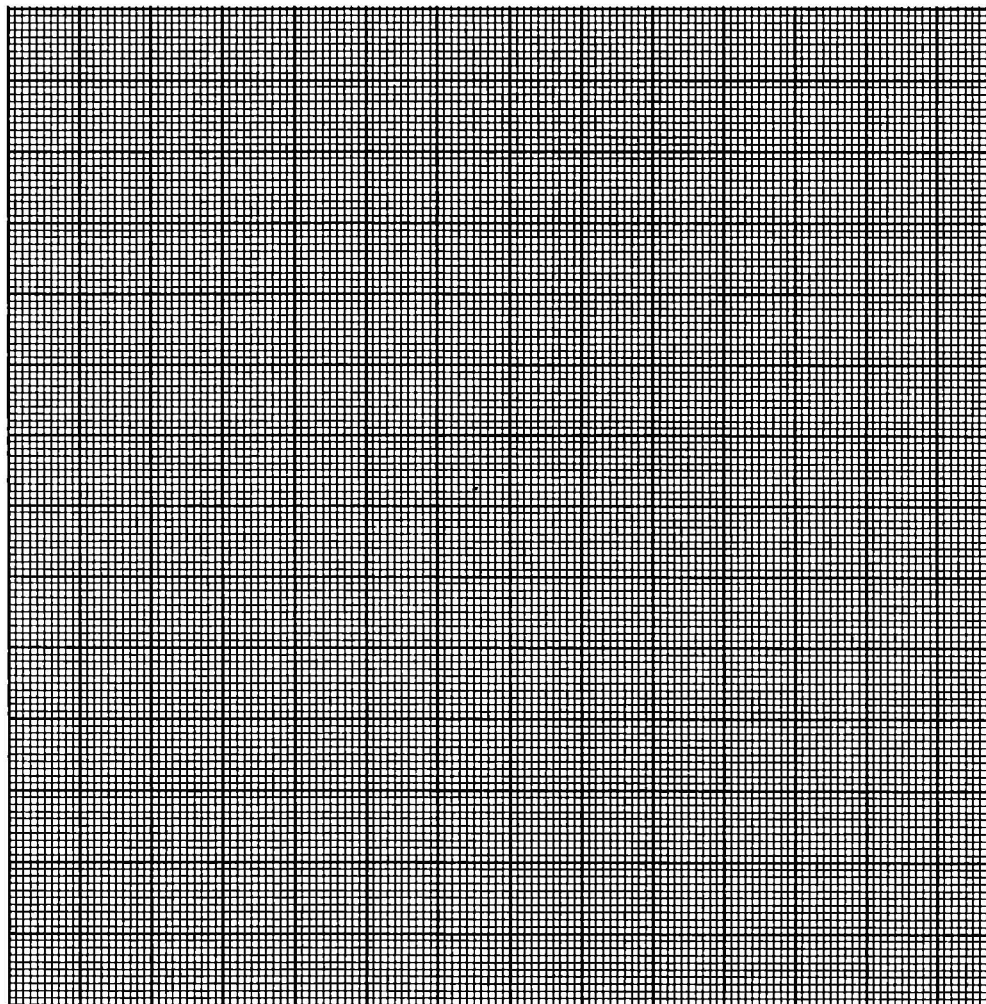
where 0, t and ∞ represents the start, current and end time, respectively.

The slope of the plot $\left(\frac{G_0 - G_t}{G_t - G_x} \right) = f(t)$ allows determining the rate constant k_2 .

6.2. Working Procedure

Make a 0.02 M solution of ethyl acetate in water, in a standard 100 mL flask.

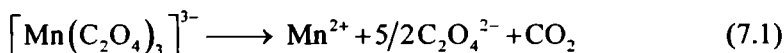
Equal volumes of 0.02 M ethyl acetate and 0.02 M NaOH will be added to the conductometer cell, and thoroughly mixed. Record the mixture conductance at t_0 . Then record the conductance corresponding to 10, 20, ... minutes until no significant change between two consecutive data is observed – G_∞ .



7. Kinetics of Oxalo-Manganese Complex Decomposition

7.1. Theoretical Background

The oxalo-manganese complex ion decomposes via the following stoichiometric equation:



The reaction can be followed by measuring the absorbance of the complex ion (brown-violet coloured); the bivalent manganese ion is light-pink coloured. Its absorbance variation is recorded at the wavelength corresponding to the absorption peak of the complex ion.

According to Lambert-Beer law, the absorbance is given by:

$$A = \epsilon \cdot c \cdot l \quad (7.2)$$

where ϵ represents the molar absorption coefficient, c is molar concentration of the chemical species, and l is the optical path length.

7.2. Working Procedure

The absorbance will be recorded at 450 nm wavelength, using 1 cm glass cell; the reference solvent is water.

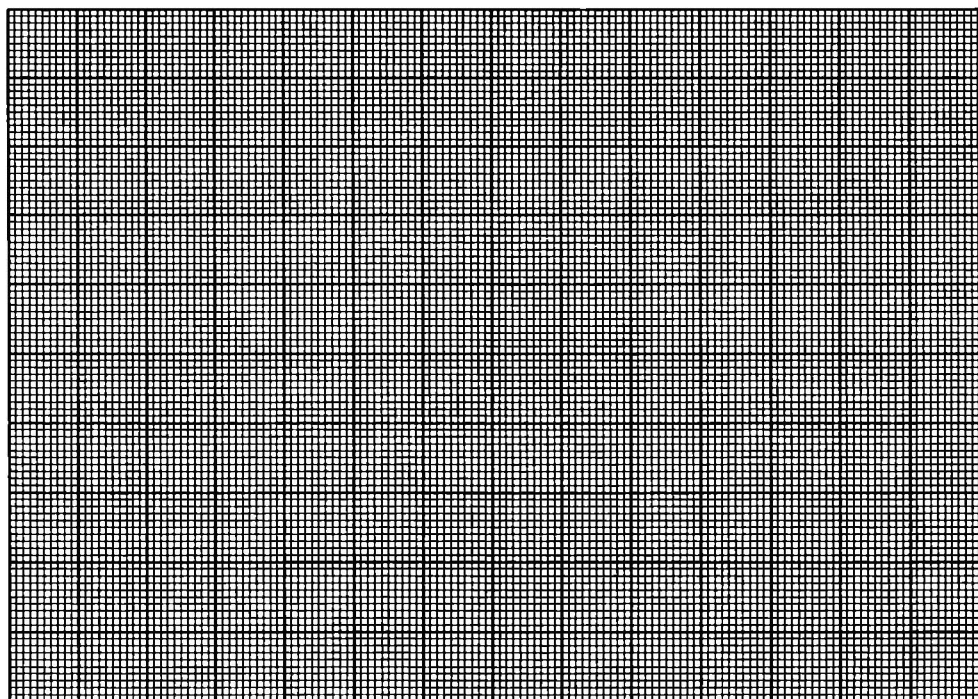
The oxalo-manganese complex will be prepared by adding 14 mL 0.1 M oxalic acid solution over 2 mL 0.1 M manganese sulphate solution, in a Berzelius flask (mixture solution **a**). The test solutions of different concentrations will be prepared as follows:

- take three 50 mL Berzelius flasks and add 12 mL, 12.25 mL, and 12.5 mL of water, respectively;
- take three samples of 2 mL from the mixture solution **a** and add them to each Berzelius flask;

- from the 0.01 M KMnO_4 bulk vessel the respective volume of solution will be taken and added to the first test solution to give 15 mL volume (1 mL); **this step will be performed only when the spectrophotometer is ready**; when the reaction starts – the moment of adding 0.01 M KMnO_4 solution – the chronometer will be started, and as soon as possible, fill the spectrophotometer cell with the test solution and record the initial absorbance of the complex ion; then record the absorbance variation at a convenient time interval (between 1 and 3 minutes), until full consumption of the reactants;
- repeat the last step with the other two test solutions.

From the $A=f(t)$ plots the half-time of each test solutions will be determined, and the rate constant will be calculated, knowing that the first order rate constant is:

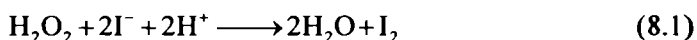
$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \quad (7.3)$$



8. Determination of the Rate Constant of the Reaction between Hydrogen Peroxide and Kalium Iodide in Acid Medium

8.1. Theoretical Background

The reaction between hydrogen peroxide and kalium iodide in acid medium is a complex one, the global equation being:



whose differential form of the reaction rate is:

$$\frac{dx}{dt} = k \cdot [\text{H}_2\text{O}_2] \cdot [\text{I}^-] \quad (8.2)$$

where x is the volume reaction extent, $\left(\frac{\xi}{V}\right)$, and the rate constant, k , depends on the proton concentration in the reaction medium. For excess concentrations of kalium iodide and acid, (8.2) becomes:

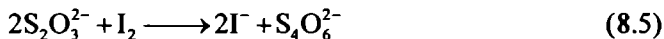
$$\frac{dx}{dt} = k_1 \cdot [\text{H}_2\text{O}_2] \quad (8.3)$$

which after integration, gives:

$$\ln \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t} = k_1 \cdot t \quad (8.4)$$

where $[\text{H}_2\text{O}_2]_0$ represents the initial concentration of the hydrogen peroxide, $[\text{H}_2\text{O}_2]_t$ is the concentration of the hydrogen peroxide at time t , and k_1 is the pseudo-first order rate constant.

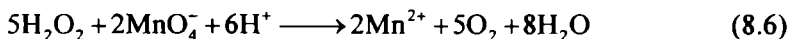
The reaction is easily monitored by titration of the resulting molecular iodine with natrium tiosulphate, in the presence of starch, according to the following stoichiometric equation:



Because the reaction is relatively fast, it cannot be followed by sampling at known time intervals from the reaction volume and titration of the aliquot. For this reason, one applies a chronometric method consisting in the record of the time corresponding to the consumption of a certain volume of the titration agent – natrium tiosulphate – by the iodine released within the reaction medium. It is necessary to add a known volume of natrium tiosulphate to the reaction medium, and record the time necessary for its consumption, i.e. the time for the blue coloration of the medium, as a result of the complex formation between iodine and pre-added starch. The quantity of added natrium tiosulphate corresponds to the quantity of hydrogen peroxide, which will be consumed within the next time interval.

8.2. Working Procedure

One prepares a 0.5 M solution of hydrogen peroxide, by mixing 7.5 mL of 3% H₂O₂ bulk solution with 125 mL of distilled water. The exact concentration of hydrogen peroxide solution will be determined by titration with 0.02 M KMnO₄ solution, in acid medium (the mixture of 25 mL of 0.5 M hydrogen peroxide solution and 3 mL of 3 M H₂SO₄ will be neutralized by the KMnO₄ solution until light pink coloration appears), according to the following redox reaction:



The reaction mixture will be prepared as follows:

- add 150 mL of distilled water, 20 mL of 1 M kalium iodide, 10 mL of 3 M sulphuric acid, 5 mL of 5% starch, and 2 mL of 0.1 M natrium tiosulphate, in a 250 mL Erlenmeyer flask;
- make sure that the chronometer is readily available;
- thoroughly mix and add 20 mL of hydrogen peroxide with the previously determined concentration; start the chronometer.

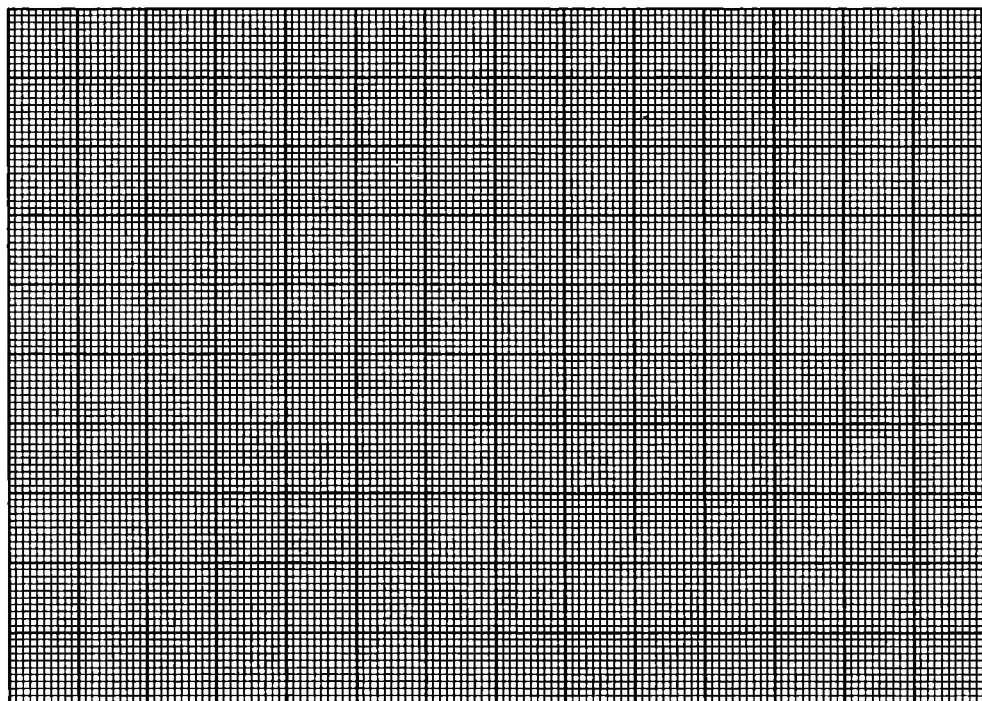
When the reaction mixture turns into blue, record the time and quickly add another 2 mL of 0.1 M natrium tiosulphate. This step will be 12÷15 times repeated.

The concentration of the non-reacted hydrogen peroxide will be calculated as follows:

- initial concentration: $[H_2O_2]_0 = \frac{n_0}{V_R}$, $[moles \times L^{-1}]$, where n_0 is the number of moles of H_2O_2 within the 20 mL solution, and V_R is the reaction volume, in litres ($V_0 = 0.207$ L);
- after the first addition of 2 mL tiosulphate, the number of moles of tiosulphate is $n_{Na_2S_2O_3} = 2 \cdot 10^{-4}$, which corresponds to $1 \cdot 10^{-4}$ moles of hydrogen peroxide consumed;
- taking into account that the reaction volume is also modified, the actual concentration of the hydrogen peroxide will be:

$$[H_2O_2]_1 = \frac{n_0 - 10^{-4}}{V_R} = \frac{n_0 - 10^{-4}}{0.209}, [moles \times L^{-1}].$$

Finally, the plot of $\ln[H_2O_2]_t = f(t)$ allows determination of the pseudo-first order rate constant.



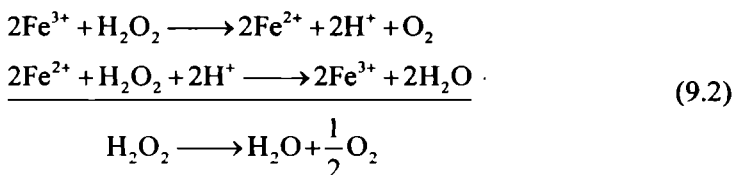
9. The Catalytic Effect of Iron (III) Chloride on the Decomposition of Hydrogen Peroxide. Catalyst Promotion and Inhibition

9.1. Theoretical Background

At room temperature, the hydrogen peroxide slowly decomposes and molecular oxygen evolves, according to the following stoichiometric equation:



The reaction rate is significantly increased in the presence of iron (III) chloride, which acts as a decomposition catalyst. The mechanism contains two steps:



The global process shows a first order kinetics. The differential form of the kinetic equation is:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k \cdot [\text{H}_2\text{O}_2] \quad (9.3)$$

and, consequently, its integral form is:

$$\ln \left\{ \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t} \right\} = k \cdot t \quad (9.4)$$

The rate of the catalytic reaction can be increased or lowered by adding copper (II) chloride or acetanilide, respectively, their action being directed towards the catalyst.

A simple and convenient method to follow the hydrogen peroxide decomposition consists in measuring the oxygen evolved at different reaction times. The initial quantity of hydrogen peroxide corresponds to the total volume of the evolved oxygen, V_{∞} , and, the quantity of hydrogen peroxide decomposed at time t corresponds to the volume of the oxygen measured at that time, V_t . The integral form of the kinetic equation (9.4) can be rewritten as:

$$\ln\left(\frac{V_{\infty}}{V_{\infty}-V_t}\right)=k \cdot t \quad (9.5)$$

where the difference $V_{\infty} - V_t$ corresponds to the quantity of the unreacted hydrogen peroxide at time t .

9.2. Working Procedure

The reaction flask is provided with an air-tightening stopper, and an upper-sided glass arm that allows connection to an U-shaped water column for gas volume measurements. The water column will be reset to zero by the help of a rubber pear.

9.2.1. The Catalytic Activity of Iron (III) Chloride

Make sure that a chronometer is readily available. Take 3 mL of 3% hydrogen peroxide solution and 1 mL of 0.05 M ferric chloride solution, and add them to the reaction flask. Plug-in the air-stopper, thoroughly mix the reaction flask, and start the chronometer. Within the interval of 30 minutes from start at least 15 gas volume measurements will be made by uprising the reaction flask until the level of the solution surface equals that of the water surface from the nearest U-shaped water column. Make sure that the reaction mixture is continuously mixed between the measurements.

The total volume of the evolved oxygen, V_{∞} , will be measured when no more gas bubbles is observed. Sinking the reaction flask in a hot water-filled Berzelius can accelerate the reaction, but the gas volume measurement will be performed only at room temperature, allowing the reaction flask to reach the equilibrium temperature.

9.2.2. Promoting and Inhibiting the Iron (III) Chloride Catalyst

The copper (II) chloride promotes the catalytic activity of the ferric chloride. In order to investigate this effect, the reaction mixture will be: 3 mL of 3% hydrogen peroxide solution, 1 mL of 0.05 M ferric chloride solution, and 1 mL 0.005 M copper (II) chloride solution.

Acetanilide stands at the opposite side; in order to investigate the inhibiting effect of the acetanilide on the catalyst, one has to add 0.005 M acetanilide solution to the catalysed reaction mixture.

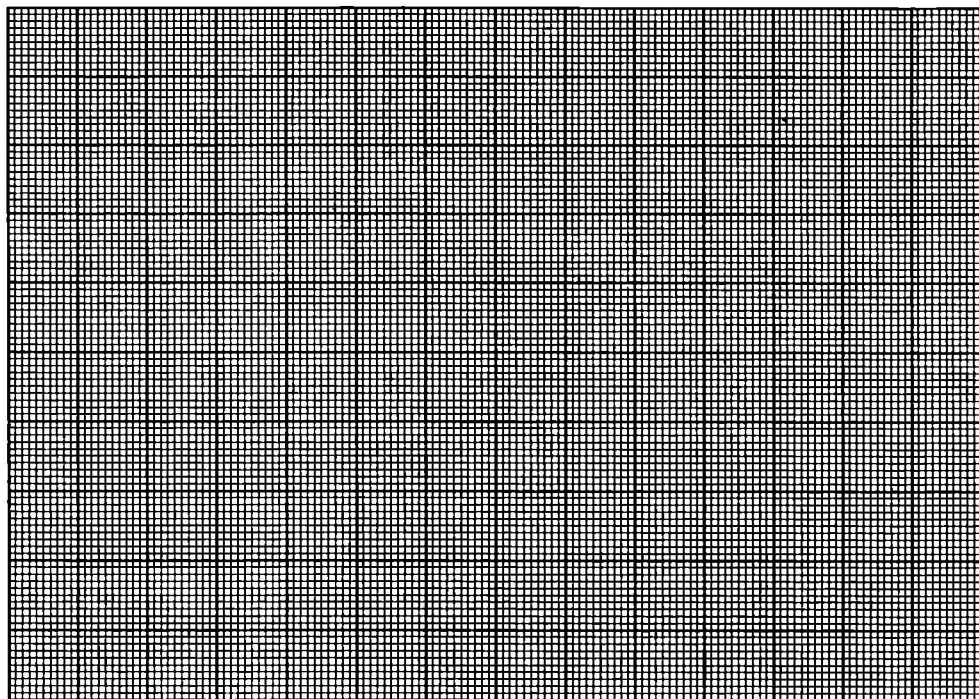
The experiments follow the same procedure as in § 9.2.1.

9.3. Data Reporting

Each of the 3 datasets will be drawn on millimetre sheets, as $\ln\left(\frac{V_\infty}{V_\infty - V_t}\right) = f(t)$.

The slopes of the linear dependencies are the first order rate constants for the decomposition of hydrogen peroxide.

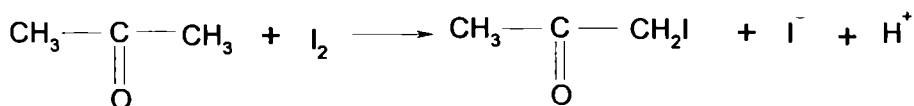
The values will be compared and the tendencies will be explained regarding actual experimental details.



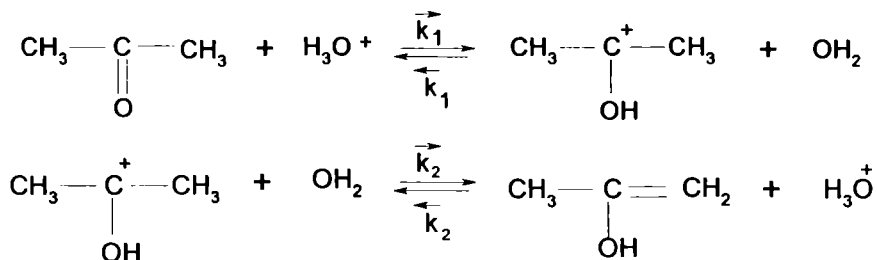
10. Determination of the Rate Constant of the Reaction between Acetone and Molecular Iodine in Acidic Medium

10.1. Theoretical Background

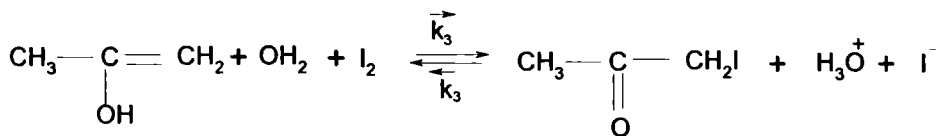
The global equation of the reaction between acetone and molecular iodine is:



Both acids and bases can catalyse this reaction. In acid medium, the presence of hydrogen ions may cause a tautomeric transformation of acetone in enole:



The resulted enole is consumed either in the reverse reaction ($\bar{v}_1$) in order to reform acetone, or in the reaction with molecular iodine ($\bar{v}_3$), giving an iodinated product.



The reaction advances, the concentration of hydrogen ions increases and the overall process becomes autocatalytic. Since in the previous reaction sequence both cation and enole are active intermediates, the net rates of consecutive steps (1, 2, 3)

become equal. Thus, the entire process is described by a single reaction rate v_R , equal to each step rate (1, 2, 3):

$$v_R = \vec{v}_1 - \vec{v}_1 = \vec{v}_2 - \vec{v}_2 = \vec{v}_3 - \vec{v}_3 \quad (10.1)$$

It is convenient to write:

$$v_R = \tilde{k}_1 [\text{acetone}] \cdot [\text{H}_3\text{O}^+] - \tilde{k}_1 [\text{cation}] \cdot [\text{H}_2\text{O}] \quad (10.2)$$

On account of the fact that:

$$[\text{cation}] \ll [\text{acetone}], [\text{H}_3\text{O}^+] \quad (10.3)$$

the expression of the kinetic equation becomes:

$$v_R = \tilde{k}_1 [\text{acetone}] \cdot [\text{H}_3\text{O}^+] \quad (10.4)$$

The differential form of the kinetic equation is:

$$\frac{dx}{dt} = k_1 [\text{acetone}] \cdot [\text{H}_3\text{O}^+] \quad (10.5)$$

which after integration gives:

$$k_1 = \frac{1}{(a+b) \cdot t} \left[\ln \frac{(b+x)}{(a-x)} + \ln \frac{a}{b} \right] \quad (10.6)$$

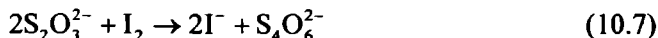
where: a = initial concentration of acetone (moles $\times$ L⁻¹)

b = initial concentration of hydrochloric acid (moles $\times$ L⁻¹)

t = reaction time (min)

x = volume reaction extent (moles $\times$ L⁻¹)

The value of x can be easily measured by titration of unconsumed iodine with sodium tiosulphate in the presence of starch, according to the following stoichiometric equation:



10.2. Working Procedure

Mix 10 mL 0.1 N iodine (in 4% kalium iodide solution) with 5 mL of 2N hydrochloric acid in a 100 mL volumetric flask and add distilled water until the ring mark is reached. Transfer the content in a polished plug flask and sink the flask directly in a thermostat. At the working temperature, add 0.75 mL acetone

and start the timer or note the time. Pull out at once a 10 mL sample from the reaction mixture and pour it in an Erlenmeyer flask containing 10 mL sodium hydro-carbonate solution (which will stop the reaction).

Titrate to the sample with 0.01N sodium tiosulphate (prepared by diluting the 0.1N stock solution) in the presence of starch, until the blue colour of iodine-starch complex turns to light blue. Remove other 10 mL samples at time intervals in which evident decreasing of iodine concentration can be observed. The next samples will be treated similar to first one. The supervisor establishes the work temperature and sampling intervals.

10.3. Data Reporting

The rate constant will be calculated with eqn. (10.6). The concentration of hydrogen ions will be calculated from the concentration of hydrochloric acid, and acetone concentration can be determined using the molecular mass ($M=58\text{g}\times\text{mol}^{-1}$) and the density ($\rho=0.787\text{g}\times\text{cm}^{-3}$). The volume reaction extent results from the formula:

$$x = \frac{V_0 - V_t}{10} \cdot N \quad (10.8)$$

where: V_0 = volume of sodium tiosulphate used in order to titrate the first sample (mL)

V_t = volume of sodium tiosulphate used in order to titrate the sample removed at time t (mL)

10 = sample volume (mL)

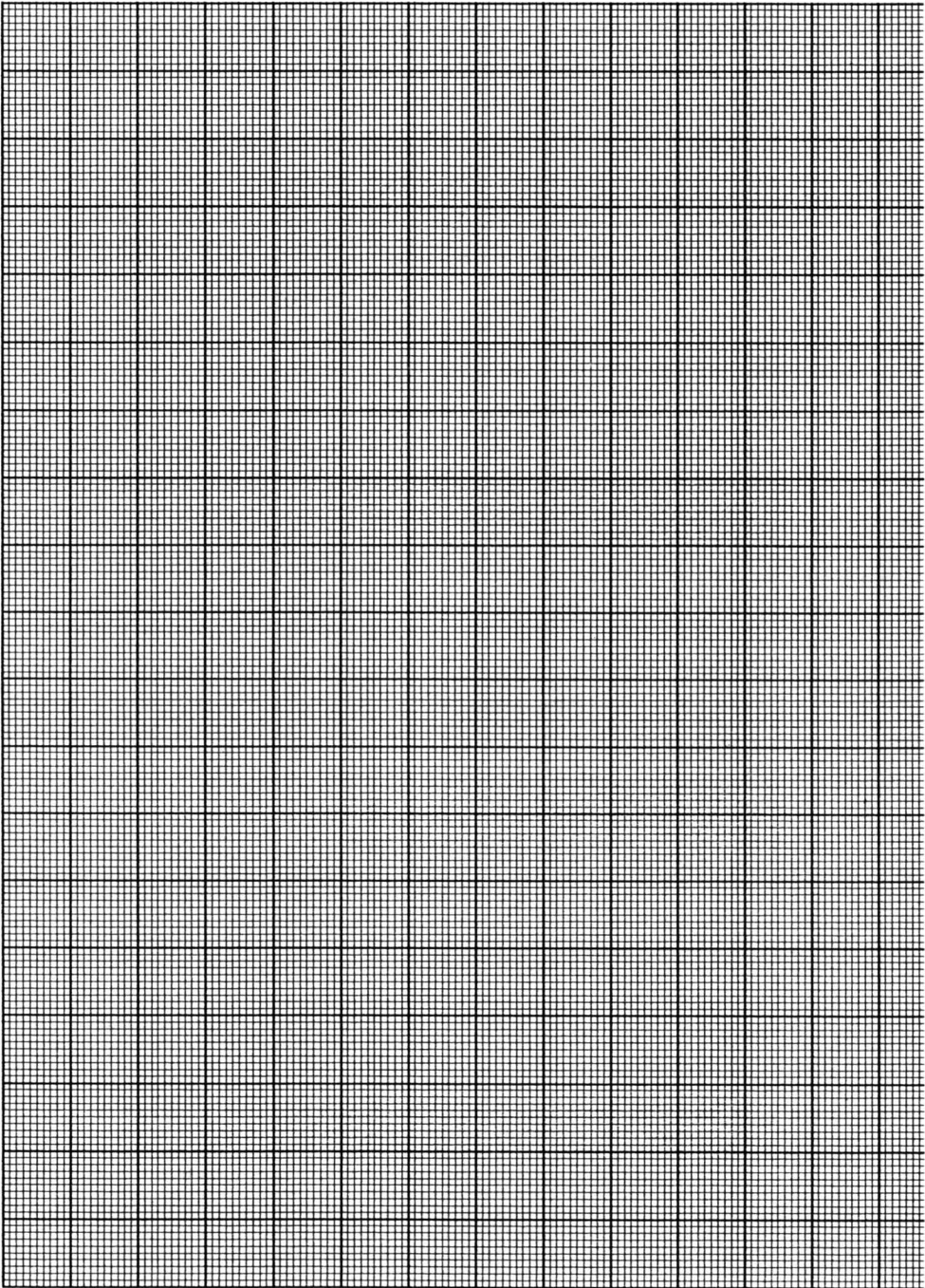
N = normal concentration of tiosulphate solution ($\text{e}_g \times \text{L}^{-1}$)

The results will be summarized in a table:

Sample No.	Time (min)	V (mL)	x ($\text{mol}\times\text{L}^{-1}$)	K ($\text{L}\times\text{mol}^{-1}\times\text{min}^{-1}$)

The average of the calculated constants will be compared to the value resulted as

slope from the plot of $\ln \frac{b+x}{a-x} = f(t)$.



11. The Effect of the Ionic Strength on the Kinetics of Ion-Ion Reactions

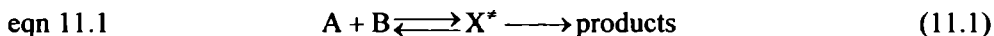
11.1. Theoretical background

The presence of ions in solution considerably changes the behaviour of a certain reaction. These effects are called salt effects because the main sources of ions are salts.

There are two kinds of salt effects:

1. Primary effects – modify the activity coefficients of the reactants and of the activated complex
2. Secondary effects – act on the nature of reactant species

One can apply the theory of transition state to account for the effects on the rate constants of reactions involving ions, which can be expressed for a bimolecular reaction as:



where $\text{X}^{\ddagger}$ is the activated complex in equilibrium with the reactants. The reaction rate is equal to decomposition rate of the activated complex:

$$r_{\text{R}} = k^{\ddagger} \cdot [\text{X}^{\ddagger}] \quad (11.2)$$

The concentration of $\text{X}^{\ddagger}$ can be calculated using the equilibrium constant $K^{\ddagger}$:

$$K_a^{\ddagger} = \frac{a_{\text{X}}}{a_{\text{A}} \cdot a_{\text{B}}} = \frac{f_{\text{X}^{\ddagger}} \cdot [\text{X}^{\ddagger}]}{f_{\text{A}} [\text{A}] \cdot f_{\text{B}} [\text{B}]} \quad (11.3)$$

where $a_j = f_j \cdot c_j$ represents the activity of species j ; f_j is the activity coefficient, depending on the ionic strength and c_j is the concentration of species j . The expression of the reaction rate is obtained introducing $[\text{X}^{\ddagger}]$ from (11.3) in (11.2).

$$r_R = k_{\text{exp}} [A][B] = k_2 [A][B] \quad (11.4)$$

$$k_2 = k^* \cdot K_a^* \cdot \frac{f_A \cdot f_B}{f_{X^*}} = k_0 \cdot \frac{f_A \cdot f_B}{f_{X^*}} \quad (11.5)$$

where k_0 is the rate constant of the reference medium (at an infinite dilution, with $f_j = 1$). The logarithmation of (11.5) leads to:

$$\ln k_2 = \ln k_0 + \ln \left(\frac{f_A \cdot f_B}{f_{X^*}} \right) = \ln k_0 + 2 \cdot z_A \cdot z_B \cdot A \cdot \frac{\sqrt{J}}{1 + \sqrt{J}} \quad (11.6)$$

The correlation between the activity coefficients and the ionic strength is given by the Debye - Hückel equation or one of its improved forms:

The following relation can be used for uni-univalent electrolytes at 25°C in water at concentrations up to 0.1M:

$$\ln f_j = -z_j^2 \cdot A \cdot \frac{\sqrt{J}}{1 + \sqrt{J}}; \quad J = \frac{1}{2} \cdot \sum c_j z_j^2 \quad (11.7)$$

where z_i is the ionic charge, J is the ionic strength, c_j is the concentration of the ion (ion-g/L) and A represents the proportionality constant.

The aim of this practical work is to verify equation (11.6) for the reaction between the green malachite and the hydroxide ion. The reaction is monitored using a spectrophotometric method at $\lambda = 616$ nm, where the reaction products have no absorption, being colourless. The reaction follows a second order kinetics, but in excess of hydroxide ions, it can be considered as a pseudo-first order reaction:

$$\ln \left(\frac{c_0}{c_t} \right) = k_1 \cdot t \quad (11.8)$$

where c_0 is the initial concentration of green malachite and c_t its concentration at the moment t . Since the Lambert-Beer law is valid in the working range, (11.8) becomes (in the logarithmic form) as it follows:

$$\ln A_t = \ln A_0 - k_1 \cdot t \quad (11.9)$$

where A_0 and A_t are the absorbances recorded at times 0, and t .

11.2. Experimental Part

11.2.1. Materials and apparatus

- Spectrophotometer, glass cuvettes of 3 cm optical way;
- Solutions: 50 mg/mL green malachite, 0.1M sodium hydroxide, 1M potassium nitrate;

- 50 mL volumetric flask, pipettes, timer.

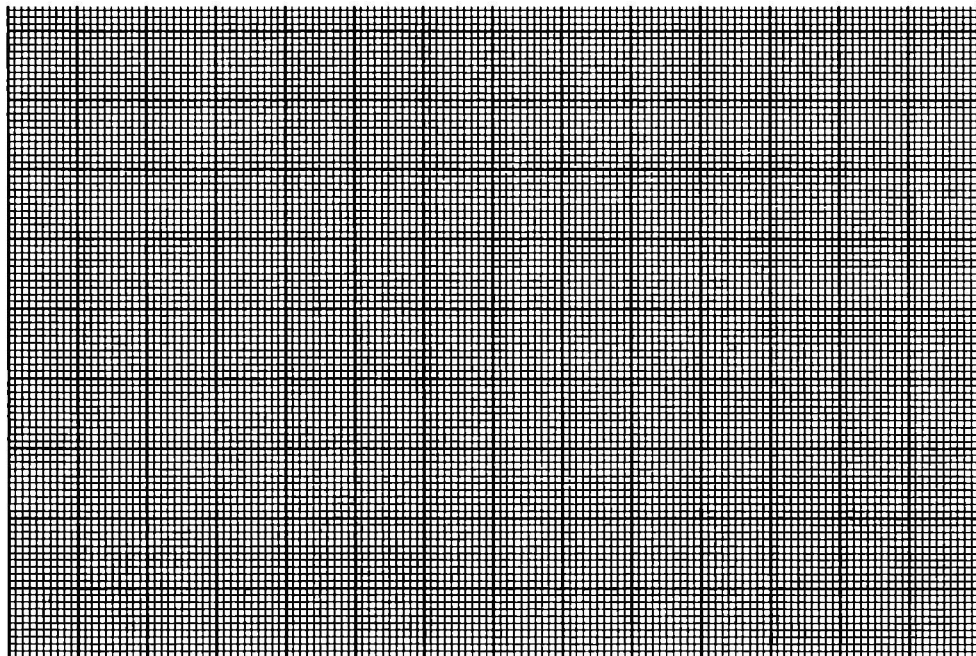
11.2.2. Working Procedure

Add 5 mL green malachite in a 50 mL volumetric flask and fill the flask with distilled water to the mark. After stirring, add 1 mL 0.1M sodium hydroxide and note the time. Stir again and transfer the mixture in the cuvette. Record the absorbance from 30 to 30 seconds for 10 minutes long. Repeat the procedure for another 5 samples containing, besides the green malachite, 1, 2, 3, 4 and 5 mL potassium nitrate (added before filling with distilled water)

11.3. Data reporting

Draw the natural logarithm of the absorbance against the time, for each series of measurements. Determine the pseudo first order constant k_1 as the slope from the eqn. (11.9). Calculate k_2 (second order rate constant), $k_2 = \frac{k_1}{[\text{NaOH}]}$. Calculate the

ionic strengths using eqn. (11.7). Draw $\ln k_2 = f\left(\frac{J^{1/2}}{1 + J^{1/2}}\right)$ and compare the slope to the theoretical one $(2.446 \cdot z_A \cdot z_B)$



Part II: Seminars

1. Seminary

Exercise no. 1

What is the volume occupied by 45 g water vapours at 100°C and 0.1 atmospheres if the gas has an ideal behaviour?

$$p \cdot V = n \cdot R \cdot T$$

R:

$$n = \frac{45}{18} = 2.5; R = 0.082 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

$$V = \frac{n \cdot R \cdot T}{p} = \frac{2.5 \cdot 0.082 \cdot 373.15}{0.1} = 765 \text{ L}$$

Exercise no. 2

The evaporation of 0.11g pure saturated hydrocarbon provides a 27 ml displacement of an air column, measured in mercury filled U-shaped tube, at 26.1°C and 243 torr. What are the molecular mass and the molecular formula of the hydrocarbon?

$$p \cdot V = \frac{m}{M} \cdot R \cdot T \Rightarrow M = \frac{m \cdot R \cdot T}{p \cdot V}$$

R:

$$\left. \begin{array}{l} 1 \text{ atm} \dots\dots\dots 760 \text{ mmHg} \\ x \text{ atm} \dots\dots\dots 243 \text{ mmHg} \end{array} \right\} \Rightarrow x = \frac{243}{760} = 0.32 \text{ atm}$$

$$M = \frac{0.11 \cdot 0.082 \cdot 299.25}{0.32 \cdot 0.027} = 312 \text{ g/mol} \Leftrightarrow 14n + 2 = 312$$

$$n = \frac{310}{14} = 22 \Rightarrow \text{C}_{22}\text{H}_{46}$$

Exercise no. 3

A 1L vessel containing a gaseous compound at 25°C is emptied until the pressure becomes 0.0001 mmHg. Calculate the number of remaining molecules.

$$\left. \begin{array}{l} 1 \text{ atm} \dots\dots\dots 760 \text{ mmHg} \\ x \text{ atm} \dots\dots\dots 0.0001 \text{ mmHg} \end{array} \right\} \Rightarrow x = \frac{0.0001}{760} = 1.31 \cdot 10^{-7} \text{ atm}$$

R:

$$N' = N_A \cdot \frac{p \cdot V}{R \cdot T} = 6.023 \cdot 10^{23} \text{ mol}^{-1} \cdot \frac{1.31 \cdot 10^{-7} \text{ atm} \cdot 1 \text{ L}}{0.082 \frac{\text{L} \times \text{atm}}{\text{mol} \times \text{K}} \cdot 298.15 \text{ K}} = 3.23 \cdot 10^{15}$$

2. Seminary

Exercise no. 4

At which temperature the average square velocity of the oxygen molecule equals that of nitrogen molecule at 100°C?

$$\overline{c^2} = \frac{3 \cdot k \cdot T}{m} = \frac{3 \cdot R \cdot T}{M}$$

R:

$$\left. \begin{aligned} \overline{c_{O_2}^2} &= \frac{3 \cdot R \cdot T_{O_2}}{M_{O_2}} \\ \overline{c_{N_2}^2} &= \frac{3 \cdot R \cdot T_{N_2}}{M_{N_2}} \end{aligned} \right\} \Rightarrow T_{O_2} = \frac{T_{N_2} \cdot M_{O_2}}{M_{N_2}} = 426 \text{ K } (153^\circ \text{ C})$$

Exercise no. 5

At 287°C, Xenon possesses an average square velocity twice lower than that of the oxygen molecule under normal condition.

Requests:

- Molecular mass of Xenon;
- The velocity of the maximum number of Xenon atoms (α);
- The density of Xenon under actual condition, knowing that the pressure is 50 atmospheres.

$$\text{R: a) } \left. \begin{array}{l} \overline{c_{\text{Xe}}^2} = \frac{3 \cdot R \cdot T_{\text{Xe}}}{M_{\text{Xe}}} \\ \overline{c_{\text{O}_2}^2} = \frac{3 \cdot R \cdot T_{\text{O}_2}}{M_{\text{O}_2}} \\ 2 \cdot \overline{c_{\text{Xe}}^2} = \overline{c_{\text{O}_2}^2} \end{array} \right\} \Rightarrow M_{\text{Xe}} = \frac{2 \cdot T_{\text{Xe}} \cdot M_{\text{O}_2}}{T_{\text{O}_2}} = 131.28 \cdot 10^{-3} \text{ kg} \times \text{mol}^{-1}$$

$$\text{R: b) } \alpha = \left(\frac{2 \cdot k \cdot T}{m} \right)^{1/2} = \left(\frac{2 \cdot R \cdot T}{M} \right)^{1/2}$$

$$\alpha_{\text{Xe}}^{560\text{K}} = (70895.8)^{1/2} = 266.263 \text{ m} \times \text{s}^{-1}$$

$$\text{R: c) } P \cdot V = \frac{2}{3} \cdot N \cdot \frac{m \cdot \overline{c^2}}{2} \Leftrightarrow P = \frac{2}{3} \cdot \frac{N}{V} \cdot \frac{m \cdot \overline{c^2}}{2} \Leftrightarrow$$

$$\Leftrightarrow P = \frac{M}{V} \cdot \frac{\overline{c^2}}{3} \Leftrightarrow P = \rho \cdot \frac{\overline{c^2}}{3} \Leftrightarrow \rho = \frac{3 \cdot P}{\overline{c^2}}$$

We need average square velocity for Xenon:

$$\overline{c_{\text{Xe}}^2} = \frac{3 \cdot R \cdot T_{\text{Xe}}}{M_{\text{Xe}}} = 106.344 \text{ m}^2 \times \text{s}^{-2} \Rightarrow \rho = 142.885 \text{ kg} \times \text{m}^{-3}$$

3. Seminary

Exercise no. 6

Calculate the square root of average square velocity $\left(\overline{c^2}\right)^{\frac{1}{2}}$, the velocity of maximum probability α and the average velocity $\bar{c}$ for nitrogen molecules at 30°C. What is the order of increasing?

$$\left(\overline{c^2}_{N_2}\right)^{\frac{1}{2}} = \left(\frac{3 \cdot R \cdot T_{N_2}}{M_{N_2}}\right)^{\frac{1}{2}} = \left(\frac{3 \cdot 8.31 \frac{\text{J}}{\text{mol} \times \text{K}} \cdot 303\text{K}}{28 \cdot 10^{-3} \frac{\text{Kg}}{\text{mol}}}\right)^{\frac{1}{2}} = 519 \text{m} \times \text{s}^{-1}$$

R:

$$\alpha_{N_2} = \left(\frac{2 \cdot R \cdot T_{N_2}}{M_{N_2}}\right)^{\frac{1}{2}} = \left(\frac{2 \cdot 8.31 \frac{\text{J}}{\text{mol} \times \text{K}} \cdot 303\text{K}}{28 \cdot 10^{-3} \frac{\text{Kg}}{\text{mol}}}\right)^{\frac{1}{2}} = 424 \text{m} \times \text{s}^{-1}$$

$$\bar{c} = \left(\frac{8 \cdot R \cdot T_{N_2}}{M_{N_2}}\right)^{\frac{1}{2}} = \left(\frac{8 \cdot 8.31 \frac{\text{J}}{\text{mol} \times \text{K}} \cdot 303\text{K}}{28 \cdot 10^{-3} \frac{\text{Kg}}{\text{mol}}}\right)^{\frac{1}{2}} = 479 \text{m} \times \text{s}^{-1}$$

$$\alpha < \bar{c} < \left(\overline{c^2}\right)^{\frac{1}{2}}$$

Exercise no. 7

Calculate the fraction of oxygen molecules having an energy at least 10 KJ/mol at 0°C and at 50°C.

$$\text{R:} \quad \frac{N_E}{N} = \exp\left(-\frac{E}{RT}\right) = \exp\left(-\frac{10^4 \frac{\text{J}}{\text{mol}}}{8.31 \frac{\text{J}}{\text{mol} \times \text{K}} \cdot 273.15 \text{K}}\right) = 0.012 \quad \text{at } 0^\circ\text{C}$$

$$\frac{N_E}{N} = \exp\left(-\frac{E}{RT}\right) = \exp\left(-\frac{10^4 \frac{\text{J}}{\text{mol}}}{8.31 \frac{\text{J}}{\text{mol} \times \text{K}} \cdot 323 \text{K}}\right) = 0.024 \quad \text{at } 50^\circ\text{C}$$

Exercise no. 8

Calculate the number of collisions between oxygen molecules and nitrogen molecules from air, Z_{AB}^* (mol·dm⁻³·s⁻¹) at 25°C and 1 atm (knowing that the air contents 21% O₂ and 79% N₂ in volume percents) and the collision diameter ($r_A + r_B$) is equal to $3.70 \cdot 10^{-10}$ m.

$$\begin{aligned} \text{R:} \quad Z_{AB}^* (\text{mol} \times \text{dm}^3 \times \text{s}^{-1}) &= \frac{Z_{AB} (\text{m}^3 \text{s}^{-1})}{N_0 (\text{mol}^{-1})} \cdot 10^{-3} = \\ &= Z_0^* (\text{dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1}) \cdot C_{\text{O}_2} (\text{mol} \times \text{dm}^{-3}) \cdot C_{\text{N}_2} (\text{mol} \times \text{dm}^{-3}) \end{aligned}$$

$$\text{where:} \quad Z_0^* (\text{dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1}) = Z_0 (\text{m}^3 \times \text{s}^{-1}) \cdot N_0 (\text{mol}^{-1}) \cdot 10^3$$

$$Z_0 (\text{m}^3 \times \text{s}^{-1}) = \pi \cdot (r_{\text{O}_2} + r_{\text{N}_2})^2 \cdot \bar{c}_{\text{rel}}$$

$$(\bar{c}_{\text{rel}})^2 = (\bar{c}_{\text{O}_2} + \bar{c}_{\text{N}_2})^2 \cong \bar{c}_{\text{O}_2}^2 + \bar{c}_{\text{N}_2}^2 \Rightarrow \bar{c}_{\text{rel}} = (\bar{c}_{\text{O}_2}^2 + \bar{c}_{\text{N}_2}^2)^{\frac{1}{2}} \Rightarrow$$

and:

$$Z_0 = \pi \cdot (r_{\text{O}_2} + r_{\text{N}_2})^2 \cdot (\bar{c}_{\text{O}_2}^2 + \bar{c}_{\text{N}_2}^2)^{\frac{1}{2}} = \pi (r_{\text{O}_2} + r_{\text{N}_2})^2 \cdot \left[\frac{8RT}{\pi} \cdot \left(\frac{1}{M_{\text{O}_2}} + \frac{1}{M_{\text{N}_2}} \right) \right]^{\frac{1}{2}} \Rightarrow$$

$$Z_0 = 2.7 \cdot 10^{-16} \text{ m}^3 \times \text{s}^{-1}; Z_0^* = 2.7 \cdot 10^{-16} \cdot 6.023 \cdot 10^{23} \cdot 10^3 = 1.62 \cdot 10^{11} \text{ dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1}$$

$$C_{\text{O}_2} = \frac{0.21}{0.082 \cdot 298} = 8.59 \cdot 10^{-3} \text{ mol} \times \text{dm}^{-3}$$

$$C_{\text{N}_2} = \frac{0.79}{0.082 \cdot 298} = 32 \cdot 10^{-3} \text{ mol} \times \text{dm}^{-3}$$

$$Z_{\text{AB}}^* = 1.62 \cdot 10^{11} \cdot 8.59 \cdot 10^{-3} \cdot 32 \cdot 10^{-3} = 4.45 \cdot 10^7 \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1}$$

4. Seminary

Exercise no. 9

Calculate shock index and mean free path for the hydrogen molecule in normal condition (0°C , 1 atm); $\sigma_{\text{H}_2} = 2.3 \text{ \AA}$ – diameter.

$$\text{R: } \left. \begin{aligned} Z_{1,n} &= \sqrt{2} \cdot \pi \cdot \sigma^2 \cdot \bar{c} \cdot n \\ n &= \frac{N}{V} \cdot \frac{N_0}{N_0} = \frac{N_0}{V} \cdot m \\ \bar{c} &= \left(\frac{8 \cdot R \cdot T}{\pi \cdot M} \right)^{1/2} \end{aligned} \right\} \Rightarrow \left\{ \begin{aligned} Z_{1,n} &= \sqrt{2} \cdot \pi \cdot (2.3 \cdot 10^{-10} \text{ m})^2 \cdot \\ &\left(\frac{8 \cdot 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 273 \text{ K}}{\pi \cdot 2 \cdot 10^{-3} \frac{\text{kg}}{\text{mol}}} \right)^{1/2} \cdot \\ &\frac{6.023 \cdot 10^{23} \frac{\text{molecules}}{\text{mol}}}{22.4 \cdot 10^{-3} \frac{\text{m}^3}{\text{mol}}} \end{aligned} \right.$$

$$Z_{1,n} = 1.074 \cdot 10^{10} \text{ s}^{-1}$$

$$\bar{l} = \frac{\bar{c}}{Z_{1,n}} = 1.582 \cdot 10^{-7} \text{ m}$$

Exercise no. 10

Calculate the pressure of the hydrogen, enclosed in a sphere-shaped flask of 1 litter volume, so that the mean free path equals the flask dimensions; $\sigma_{\text{H}_2} = 2.3 \text{ \AA}$; $T = 27^{\circ}\text{C}$.

$$\left. \begin{aligned}
 \bar{l} &= \frac{\bar{c}}{Z_{1,n}} = \frac{1}{\sqrt{2} \cdot \pi \cdot \sigma^2 \cdot n} \\
 Z_{1,n} &= \sqrt{2} \cdot \pi \cdot \sigma^2 \cdot \bar{c} \cdot n \\
 \text{R: } n &= \frac{N_0}{V} \cdot m = \frac{N_0 \cdot P}{R \cdot T} \\
 v_{\text{sphere}} &= \frac{4 \cdot \pi \cdot r^3}{3} \\
 d &= \bar{l} = 2 \cdot r
 \end{aligned} \right\} \Rightarrow \left\{ \begin{aligned}
 P &= \frac{R \cdot T}{\sqrt{2} \cdot \pi \cdot \sigma^2 \cdot N \cdot \bar{l}} \\
 &= \frac{8.31 \frac{\text{J}}{\text{mol} \times \text{K}} \cdot 300\text{K}}{\sqrt{2} \cdot \pi \cdot (2.3 \cdot 10^{-10} \text{m})^2 \cdot 6.023 \cdot 10^{23} \frac{\text{molecule}}{\text{mol}} \cdot 0.124 \text{m}} \\
 &= 0.142 \text{Pa}
 \end{aligned} \right.$$

Exercise no. 11

For air (vol 80% N₂, 20% O₂), at 1 atmosphere and 25 degrees Celsius, calculate the following quantities ($\sigma_{\text{O}_2} = 3.61 \text{ \AA}$; $\sigma_{\text{N}_2} = 3.8 \text{ \AA}$):

a) $Z_{n_{\text{O}_2}, n_{\text{N}_2}} = ?$

b) $Z_{n_{\text{N}_2}, n_{\text{N}_2}} = ?$

$$Z_{n_1, n_2} = \sigma_{1,2}^2 \cdot \left[8 \cdot \pi \cdot R \cdot T \cdot \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{\frac{1}{2}} \cdot n_1 \cdot n_2$$

$$\sigma_{1,2}^2 = \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2$$

R: a)

$$n = \frac{N_0}{V} \cdot m$$

$$V^{298\text{K}} = 24.451 \cdot 10^{-3} \text{m}^3$$

$$n_{\text{O}_2} = 4.926 \cdot 10^{24} \frac{\text{molecules}}{\text{m}^3}$$

$$n_{\text{N}_2} = 1.97 \cdot 10^{25} \frac{\text{molecules}}{\text{m}^3}$$

$$Z_{n_1, n_2} = (3.8 \cdot 10^{-10})^2 \cdot \left[16 \cdot 3.14 \cdot 8.31 \cdot 298 \cdot \frac{1}{28 \cdot 10^{-3}} \right]^{\frac{1}{2}} \cdot (1.97 \cdot 10^{25})^2 = 1.18 \cdot 10^{34} \text{m}^{-3} \times \text{s}^{-1}$$

5. Seminary

Exercise no. 12

The coefficient of internal friction in normal conditions (1atm, 0°C) has the value: $\eta = 8.8 \cdot 10^{-5} \text{ P}$. Calculate the diameter of hydrogen molecule.

R: The kinetic – molecular significance of η is:

$$\eta = \frac{n \cdot m \cdot \bar{c}_{H_2} \cdot \bar{l}}{3} \quad \text{where } n = \frac{N_{H_2}}{V} \quad \text{and } m = \frac{M_{H_2}}{N_0}$$

$$\bar{c}_{H_2} = \left(\frac{8RT}{\pi M_{H_2}} \right)^{\frac{1}{2}} \quad \text{and } \bar{l} = \frac{\bar{c}_{H_2}}{Z_{1\Lambda\Lambda}} = \frac{\bar{c}_{H_2}}{\pi \cdot \sigma^2 \cdot \bar{c}_{rel} \cdot n}$$

$$\bar{c}_{rel} = \left(2 \cdot \bar{c}_{H_2}^2 \right)^{\frac{1}{2}} = \sqrt{2} \cdot \bar{c}_{H_2} \Rightarrow \bar{l} = \frac{1}{\sqrt{2} \cdot \pi \cdot \sigma^2 \cdot n} \Rightarrow$$

$$\eta = \frac{m \cdot \bar{c}_{H_2}}{3\sqrt{2} \cdot \pi \cdot \sigma^2} \Rightarrow \sigma = \sqrt{\frac{m \cdot \bar{c}_{H_2}}{3\sqrt{2} \cdot \pi \cdot \eta}} = 2.3 \cdot 10^{-10} \text{ m}$$

Exercise no. 13

Calculate the free energy difference at 25°C due to a galactose gradient across a membrane, if the concentration on side 1 is 2 mM and the concentration on side 2 is 10 mM.

$$\begin{aligned} \mathbf{R:} \quad \Delta G_{diff} &= RT \cdot \ln \frac{[C_2]}{[C_1]} = 8.31 \text{ J} \times \text{mol}^{-1} \times \text{K}^{-1} \cdot 298 \text{ K} \cdot \ln \frac{10 \cdot 10^{-3} \text{ M}}{2 \cdot 10^{-3} \text{ M}} \\ &= 4000 \text{ J} \times \text{mol}^{-1} = 4 \text{ kJ} \times \text{mol}^{-1} \end{aligned}$$

Exercise no. 14

Consider a phospholipid vesicle containing 10 mM Na^+ ions. The vesicle is bathed in a solution that contains 52 mM Na^+ ions, and the electrical potential difference across the vesicle membrane is: $\Delta\varepsilon = \varepsilon_{\text{outside}} - \varepsilon_{\text{inside}} = -30\text{mV}$. What is the standard free energy at 25°C for Na^+ ions?

$$\Delta G = \Delta G^0 + RT \cdot \ln \frac{C_2}{C_1} \Rightarrow \Delta G^0 = \Delta G - RT \cdot \ln \frac{C_2}{C_1} = -z \cdot F \cdot \Delta\varepsilon - RT \ln \frac{C_2}{C_1} =$$

$$\begin{aligned} \mathbf{R:} &= - \left[(+1) \cdot 96490 \text{ J} \times \text{V}^{-1} \times \text{mol}^{-1} \cdot (-30 \cdot 10^{-3} \text{ V}) + 8.31 \text{ J} \times \text{mol}^{-1} \times \text{K}^{-1} \cdot 298 \text{ K} \cdot \ln \frac{52 \text{ mM}}{10 \text{ mM}} \right] = \\ &= -1.19 \cdot 10^3 \text{ J} \times \text{mol}^{-1} \end{aligned}$$

6. Seminary

Exercise no. 15

Phospholipid lateral motion in membranes is characterized by a diffusion coefficient of about $1 \cdot 10^{-8} \text{ cm}^2 \times \text{s}^{-1}$. The distance traveled in two dimensions (in the membrane) in a given time is $r = (4 \cdot D \cdot t)^{1/2}$, where r is the distance traveled in centimeters, D is the diffusion coefficient, and t is the time during which the diffusion occurs. Calculate the distance traveled by a phospholipid in a bilayer in 10 ms.

$$D = 1 \cdot 10^{-8} \text{ cm}^2 \Rightarrow t = 10 \text{ ms} = 10 \cdot 10^{-3} \text{ s}$$

R:

$$r = \sqrt{4 \cdot D \cdot t} = \sqrt{4 \cdot 10^{-8} \cdot 10^{-2}} = 2 \cdot 10^{-7} \text{ m}$$

Exercise no. 16

Protein lateral motion is much slower than that of lipids. Also, some membrane proteins can diffuse freely through the membrane, whereas others are bound or anchored to other protein structures in the membrane.

The diffusion coefficient for the membrane protein fibronectin is approximately $0.7 \cdot 10^{-12} \text{ cm}^2 \times \text{s}^{-1}$, whereas that for rhodopsin is $3 \cdot 10^{-9} \text{ cm}^2 \times \text{s}^{-1}$. Calculate the distance traversed by each of these proteins in 10 ms.

R:
$$r = \sqrt{4 \cdot D \cdot t}$$

For fibronectin: $r = \sqrt{4 \cdot 0.7 \cdot 10^{-16} \text{ m}^2 \times \text{s}^{-1} \cdot 10^{-2} \text{ s}} = 1.67 \cdot 10^{-9} \text{ m};$

For rhodopsin: $r = \sqrt{4 \cdot 3 \cdot 10^{-13} \text{ m}^2 \times \text{s}^{-1} \cdot 10^{-2} \text{ s}} = 110 \cdot 10^{-9} \text{ m}$

Exercise no. 17

Assume that an Emperor penguin's foot has an area 0.005 m^2 and is in good thermal contact with the Antarctic ice at a temperature of -45°C . Their blood vessels within their feet are assumed to be 2 mm above the ground, and keep the interior of their feet at a steady 35°C . If the thermal conductivity is $\lambda = 0.06 \text{ J}\times\text{s}^{-1}\times\text{m}^{-1}\times\text{K}^{-1}$, what is the rate of heat flow out of their feet?

$$\begin{aligned} \text{R: } \frac{dQ}{dt} &= -\lambda \cdot S \cdot \text{grad} T = -6 \cdot 10^{-2} \text{ J}\times\text{s}^{-1}\times\text{m}^{-1}\times\text{K}^{-1} \cdot 5 \cdot 10^{-3} \text{ m}^2 \cdot \frac{308\text{K} - 208\text{K}}{2 \cdot 10^{-3} \text{ m}} = \\ &= -12 \text{ J}\times\text{s}^{-1} \end{aligned}$$

7. Seminary

Exercise no. 18

For the reaction $2A + B = C$, the rate of product formation is $0.3 \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1}$.

Requests: Calculate rates of transformation for A and B and the reaction rate.

R:

$$r_u^j = \frac{dC_j}{dt} \Rightarrow r_u^B = r_u^C = 0.3 \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1};$$

$$r_u^A = 2 \cdot r_u^C = 0.6 \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1}$$

$$r_R = \frac{1}{\nu_j} \cdot \frac{dC_j}{dt} \Rightarrow r_R = r_u^C = 0.3 \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1}$$

Exercise no. 19

The experimental study of nitrogen oxide (V) decomposition (first order reaction) provides the followings data:

Time /s	0	11040	19140	31560
Conc. /(mol×dm ⁻³)	2.33	2.08	1.91	1.67

Requests:

- Calculate the average reaction rate within $0 \div 31560 \text{ s}$;
- Calculate the average rate constant and the half time;
- Calculate the concentration of reacted substance at $t = 1000 \text{ min}$.

R: a) The average rate is:

$$\bar{r} = -\frac{C_2 - C_1}{t_2 - t_1} = -\frac{1.67 - 2.33}{31560} = 2.09 \cdot 10^{-5} \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1}$$

R: b) The rate constant for a first order reaction is:

$$k = \frac{1}{t} \cdot \ln \frac{C_0}{C}$$

$$k_1 = \frac{1}{11040} \cdot \ln \frac{2.33}{1.91} = 0.9 \cdot 10^{-4} \cdot \ln 1.12 = 1.01 \cdot 10^{-5} \text{ s}^{-1}$$

$$k_2 = \frac{1}{19140} \cdot \ln \frac{2.33}{1.91} = 0.99 \cdot 10^{-5} \text{ s}^{-1}$$

so that:

$$k_3 = \frac{1}{31650} \cdot \ln \frac{2.33}{1.67} = 1.00 \cdot 10^{-5} \text{ s}^{-1}$$

$$\bar{k} = \frac{k_1 + k_2 + k_3}{3} = 1.00 \cdot 10^{-5} \text{ s}^{-1}$$

The half time can be calculated using the expression:

$$\tau_{1/2} = \frac{0.693}{k} = \frac{0.693}{10^{-5}} = 69300 \text{ s}$$

R: c) The concentration of reacted oxide is:

$$x = a \cdot (1 - e^{-kt}) = 2.33 \cdot (1 - e^{-(0.00001 \cdot 60000)}) = 1.055 \text{ mol} \times \text{dm}^{-3}$$

Exercise no. 20

For the reaction $A \rightarrow \text{Products}$, the increase of the reactant concentration of 3 times gives an increase of reaction rate of 3 times. Calculate:

a) The reaction order;

b) The reaction rate if $C_A = 0.1 \text{ mol} \times \text{L}^{-1}$ and $t_{1/2} = 693 \text{ s}$

R: a) $C_{A_2} = 3 \cdot C_{A_1} \Rightarrow r_2 = 3 \cdot r_1$

$$r_R = k \cdot C_A^n \text{ and } \left. \begin{array}{l} r_1 = k \cdot C_{A_1}^n \\ r_2 = k \cdot C_{A_2}^n \end{array} \right\} \Rightarrow \frac{r_1}{r_2} = \left(\frac{C_{A_1}}{C_{A_2}} \right)^n \Leftrightarrow \frac{1}{3} = \left(\frac{1}{3} \right)^n \Leftrightarrow n = 1$$

R: b) $r_R = k \cdot C_A$ where $k = \frac{0.693}{\tau_{1/2}} = 10^{-3} \text{ s}^{-1} \Rightarrow r_R = 10^{-4} \text{ mol} \times \text{dm}^{-3} \times \text{s}^{-1}$

8. Seminary

Exercise no. 21

The experimental study of the basic hydrolysis of ethyl acetate (when the initial concentrations of reactants are equals to $0.02 \text{ mol} \times \text{dm}^{-3}$) provides the following data:

$t/10^3 \text{ s}$	0	18	54	82.8
$[\text{Ester}] / (\text{mol} \times \text{dm}^{-3})$	0.020	0.0128	0.00744	0.00558

Requests:

- Calculate the reaction order;
- Calculate the average rate constant.

R: a) The reaction order can be determined by presuming a certain reaction order and calculate the experimental average rate constant.

The average rate constant may be calculated using the integral form of kinetic equations:

If we admit that we deal with a first order reaction, the rate constant becomes:

$$k_1^I = \frac{1}{t} \ln \frac{C_0}{C} = \frac{1}{18000} \ln \frac{0.02}{0.0128} = 0.247 \cdot 10^{-4} \text{ s}^{-1}$$

$$k_1^{II} = \frac{1}{54000} \ln \frac{0.02}{0.00744} = 0.183 \cdot 10^{-4} \text{ s}^{-1}$$

$$k_1^{III} = \frac{1}{82800} \ln \frac{0.02}{0.00558} = 0.154 \cdot 10^{-4} \text{ s}^{-1}$$

A decreasing of the rate constant value, out of limit of experimental errors can be observed. Thus, it is obvious that the reaction order has not the value one.

If we admit that we deal with a second order reaction, the rate constant may be calculated using the formula:

$$k_2^I = \frac{1}{t} \cdot \frac{x}{a \cdot (a-x)} = \frac{1}{18000} \cdot \frac{0.0072}{0.02 \cdot 0.0128} = 1.56 \cdot 10^{-3} \text{ dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1}$$

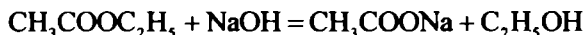
$$k_2^{II} = \frac{1}{54000} \cdot \frac{0.01256}{0.02 \cdot 0.00744} = 1.57 \cdot 10^{-3} \text{ dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1}$$

$$k_2^{III} = \frac{1}{82800} \cdot \frac{0.01442}{0.02 \cdot 0.00558} = 1.56 \cdot 10^{-3} \text{ dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1}$$

Since the three obtained values are approximately equal, we may conclude that the reaction is a second order one.

Exercise no. 22

The reaction between the sodium hydroxide and the ethyl acetate:



occurs as a second order reaction. After 180 minutes, the diminution of hydroxide concentration was equal to 0.0002 mol/L (the initial concentrations of ester and hydroxide were 0.01 mol/L and 0.005 mol/L).

Requests:

- Calculate the rate constant and the half time with respect to hydroxide;
- Calculate the concentration of the unreacted ester at $t = 500$ minutes;
- Calculate the half time and the concentration of unreacted ester at $t = 500$ min., if the initial concentrations of reactants are equal to 0.01 mol/L.

R: a)-1 The integral kinetic equation for a second order reaction is:

$$k = \frac{1}{t \cdot (a-b)} \cdot \ln \frac{b \cdot (a-x)}{a \cdot (b-x)} = \frac{1}{10800} \cdot \frac{1}{(0.01-0.005)} \cdot \ln \frac{0.005 \cdot (0.01-0.0002)}{0.01 \cdot (0.005-0.0002)} =$$

$$= 0.0185 \cdot \ln 1.021 = 3.8 \cdot 10^{-4} \text{ L} \times \text{mol}^{-1} \times \text{s}^{-1}$$

a)-2 The half time may be calculated using the expression of the rate constant:

$$\tau_{1/2} = \frac{1}{k} \cdot \frac{1}{(a-b)} \cdot \ln \frac{b \cdot \left(a - \frac{b}{2}\right)}{a \cdot \left(b - \frac{b}{2}\right)} = \frac{1}{3.8 \cdot 10^{-4}} \cdot \frac{1}{5 \cdot 10^{-3}} \ln \frac{0.005 \cdot 0.0075}{0.01 \cdot 0.0025} = 2.13 \cdot 10^5 \text{ s}$$

R: b) The integral equation of the rate constant is also used in order to calculate the concentration of unreacted ester:

$$k = \frac{1}{t} \cdot \frac{1}{(a-b)} \cdot \ln \frac{b \cdot (a-x)}{a \cdot (b-x)} \Rightarrow \ln \frac{b \cdot (a-x)}{a(b-x)} = k \cdot t \cdot (a-b) \Leftrightarrow$$

$$\ln \frac{0.005 \cdot (0.01 - x)}{0.01 \cdot (0.005 - x)} = 3.8 \cdot 10^{-4} \cdot 3 \cdot 10^4 \cdot (0.01 - 0.005) \Leftrightarrow$$

$$\ln 0.5 \cdot \frac{(0.01 - x)}{(0.005 - x)} = 0.0569 \Rightarrow \frac{0.01 - x}{0.005 - x} = 2.12 \Rightarrow x = 0.00052 \text{ mol/L}$$

The concentration of unreacted ester is $a - x = 0.01 - 0.00052 = 0.00948 \text{ mol/L}$

R: c) If the initial concentrations of reactants are equal, the integral kinetic equation becomes:

$$k = \frac{1}{t} \cdot \frac{x}{a \cdot (a-x)} \Leftrightarrow x = \frac{a^2 \cdot k \cdot t}{1 + a \cdot k \cdot t} \Rightarrow$$

$$\Rightarrow a - x = \frac{0.01}{1 + 0.01 \cdot 3.8 \cdot 10^{-4} \cdot 3 \cdot 10^4} = 0.00897 \text{ mol} \times \text{L}^{-1}$$

9. Seminary

Exercise no. 23

A chemical reaction in gaseous phase is described by the stoichiometric equation: $A = B + C$ and is practically unilateral. Show how the rate at constant volume $r_{R/V}$ can be calculated, if the volume is constant.

R: a) If the pressure is measured: P = total pressure

$n_j = \frac{V}{RT} \cdot p_j$ where p_j is the partial pressure of compound j

$$P = \frac{RT}{V_0} \cdot (n_A + n_B + n_C); \quad P_0 = \frac{RT}{V_0} \cdot n_A^0$$

$$\xi = \frac{\sum n_j - \sum n_{j_0}}{\Delta \nu_j} = \frac{V_0}{RT \cdot \Delta \nu_j} (P - P_0); \quad r_{R/V_0} = \frac{1}{V_0} \cdot \frac{d\xi}{dt} \Rightarrow$$

$$\Rightarrow r_{R/V_0} = \frac{1}{RT \cdot \Delta \nu_j} \cdot \frac{dP}{dt}$$

From the curve $P = f(t) \Rightarrow \frac{dP}{dt} \Rightarrow r_{R/V_0}$

R: b) If the product concentration is measured (by gas chromatography), then:

$$r_{R/V_0} = \frac{1}{V_0} \cdot \frac{1}{\nu_j} \cdot \frac{dn_j}{dt} = \frac{1}{V_0} \cdot \frac{1}{\nu_j} \cdot \frac{d(C_j \cdot V_0)}{dt} = \frac{1}{\nu_j} \cdot \frac{dC_j}{dt}$$

From the curve $C = f(t) \Rightarrow \frac{dC}{dt} \Rightarrow r_{R/V_0}$

Exercise no. 24

The reaction, described by the stoichiometric equation $2\text{NO} + 2\text{H}_2 = \text{N}_2 + 2\text{H}_2\text{O}$, is unilateral and takes place in gaseous phase at high temperature. Is this an elementary reaction? How can we measure the reaction rate experimentally?

R: The reaction is not elementary because:

- Do not respect the rule of minimum structure changes
- Too many molecules are involved in the reaction.
- Measurement of reaction rate:
 - If $V = \text{constant}$, $P = f(t) \Rightarrow \frac{dP}{dt} \Rightarrow r_{R/V_0} = \frac{1}{RT \cdot \Delta v_j} \cdot \frac{dP}{dt}$
 - If $P = \text{constant}$, $\ln V = f(t) \Rightarrow r_{R/V} = \frac{P_0}{RT \cdot \Delta v_j} \cdot \frac{d(\ln V)}{dt}$
 - If we measure the nitrogen concentration $r_{R/V_0} = \frac{1}{\nu_{\text{N}_2}} \cdot \frac{dC_{\text{N}_2}}{dt}$

Exercise no. 25

The reaction rate for the decomposition $\text{A} = \text{Products}$ is $9 \cdot 10^{-4} \text{ mol} \times \text{L}^{-1} \times \text{s}^{-1}$ when $C_A = 6 \cdot 10^{-4} \text{ mol} \times \text{L}^{-1}$, and $7.5 \text{ mol} \times \text{L}^{-1} \times \text{s}^{-1}$ when $C_A = 5 \cdot 10^{-4} \text{ mol} \times \text{L}^{-1}$. Calculate the reaction order and the rate constant.

R:
$$r_R = k \cdot C_A^n$$

$$\frac{r_{R_1}}{r_{R_2}} = \left(\frac{C_{A_1}}{C_{A_2}} \right)^n \Rightarrow n = 1 \Rightarrow k = \frac{r_R}{C_A} = 1.51 \cdot 10^{-3} \text{ s}^{-1}$$

10. Seminary

Exercise no. 26

What are the resemblances and the differences between an elementary reaction and a singular reaction?

R: Resemblances:

- They are described by one stoichiometric equation and one kinetic variable;
- The reaction rate shows a monotone decreasing in time.

R: Differences:

Elementary reaction	Singular reaction
– the reaction order is equal to the molecularity; – the analytical form of reaction rate is factorial; – the reaction rate can be written using the stoichiometric equation and depends only on the reactant concentrations.	– the reaction order may take negative or fractional values; – the analytical form is not always factorial; – the reaction rate may depend on the product concentrations.

Exercise no. 27

For the decomposition of N_2O_5 , $k = 1.3 \cdot 10^{-4} \text{s}^{-1}$ at $T = 313 \text{ K}$. Calculate:

- a) the reaction order;
- b) the partial pressure of N_2O_5 after 10 minutes, if the initial pressure is 0.38 Pa;
- c) the activation energy if the pre-exponential factor is $A = 4.5 \cdot 10^{13} \text{s}^{-1}$

R: a) $n = 1$ because the kinetic constant is measured in s^{-1} .

$$r_{\text{R}} = -\frac{dC_{\text{N}_2\text{O}_5}}{dt} = k \cdot C_{\text{N}_2} \Rightarrow \frac{dC_{\text{N}_2\text{O}_5}}{C_{\text{N}_2\text{O}_5}} = -k \cdot t \Rightarrow \ln\left(\frac{C_0}{C}\right) = k \cdot t$$

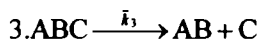
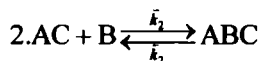
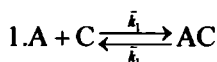
$$\text{R: b)} p_{\text{NO}_2} = \frac{n_{\text{NO}_2}}{V} \cdot RT \Rightarrow C_{\text{NO}_2} \approx p_{\text{NO}_2} \Rightarrow \ln\left(\frac{p_{\text{NO}_2}^0}{p_{\text{NO}_2}}\right) = k \cdot t \Rightarrow p_A = p^0 \cdot \exp(-k \cdot t)$$

$$\text{R: c)} \quad k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \Rightarrow E_a = RT(\ln A - \ln k) = 58.5 \text{ kJ} \times \text{mol}^{-1}$$

11. Seminary

Exercise no. 28

Write the overall kinetic equation for the 3 step catalytic sequence, assuming that
a) steps 1 and 2 are quasi equilibrated; b) AC and ABC are active intermediates.



R: a) The rate of overall process has the form:

$$\frac{d[AB]}{dt} = k_3 \cdot [ABC]$$

Assuming that step (1.) and step (2.) are quasi equilibrated, results:

$$\bar{k}_2 \cdot [AC] \cdot [B] = \bar{k}_2 [ABC] \Rightarrow$$

[AC] concentration is calculated using eq.1:

$$\bar{k}_1 [C] \cdot [A] = \bar{k}_1 \cdot [AC]$$

From the condition of catalytic centers conservation results:

$$\begin{cases} [C] + [AC] + [ABC] = [C]_0 \\ \bar{k}_2 [AC] \cdot [B] - \bar{k}_2 [ABC] = 0 \Rightarrow \\ \bar{k}_1 \cdot [A] \cdot [C] - \bar{k}_1 [AC] = 0 \end{cases}$$

$$\begin{aligned}
 [ABC] &= \frac{\bar{k}_1 \bar{k}_2 [A][B][C]_0}{\bar{k}_1 \bar{k}_2 [A] + \bar{k}_1 \bar{k}_2 [A][B] + \bar{k}_1 \bar{k}_2} \Rightarrow \\
 \frac{d[ABC]}{dt} &= \frac{k_3 \bar{k}_1 \bar{k}_2 [A][B][C]_0}{\bar{k}_1 \bar{k}_2 [A] + \bar{k}_1 \bar{k}_2 [A][B] + \bar{k}_1 \bar{k}_2} = \\
 &= k_3 \cdot \frac{K_1 K_2 [A][B][C]_0}{K_1 [A] + K_1 K_2 [A][B] + 1}
 \end{aligned}$$

R: b) We use the method of steady concentrations:

$$[AC] \ll [A], [B], [AB] \text{ and } [ABC] \ll [A], [B], [AB]$$

$$\frac{d[ABC]}{dt} = \bar{k}_2 \cdot [AC] \cdot [B] - \bar{k}_2 \cdot [ABC] - k_3 [ABC] = 0 \Rightarrow$$

$$\frac{d[AC]}{dt} = \bar{k}_1 \cdot [A] \cdot [C] - \bar{k}_1 \cdot [AC] - \bar{k}_2 \cdot [AC] \cdot [B] + \bar{k}_2 \cdot [ABC] = 0$$

And the results are:

$$\left\{ \begin{array}{l} [C] + [AC] + [ABC] = [C]_0 \\ \bar{k}_1 [A] \cdot [C] - (\bar{k}_1 + \bar{k}_2 [B]) \cdot [AC] + \bar{k}_2 \cdot [ABC] = 0 \\ + \bar{k}_2 \cdot [B] \cdot [AC] - (\bar{k}_2 + k_3) \cdot [ABC] = 0 \end{array} \right. \Rightarrow$$

$$[ABC] = \frac{\bar{k}_1 \bar{k}_2 [A][B][C]_0}{(\bar{k}_2 + k_3) \bar{k}_1 [A] + \bar{k}_1 \bar{k}_2 [A][B] + (\bar{k}_1 \bar{k}_2 + \bar{k}_1 k_3) [B]} \Rightarrow$$

$$\begin{aligned}
 \frac{d[AB]}{dt} &= \frac{k_3 \bar{k}_1 \bar{k}_2 [A][B][C]_0}{(\bar{k}_2 + k_3) \bar{k}_1 [A] + \bar{k}_1 \bar{k}_2 [A][B] + (\bar{k}_1 \bar{k}_2 + \bar{k}_1 k_3) [B]} = \\
 &= \frac{k_3 \bar{k}_1 \bar{k}_2 [A][B][C]_0}{(\bar{k}_2 + k_3)(\bar{k}_1 [A] + \bar{k}_1 [B]) + \bar{k}_1 \bar{k}_2 [A][B]}
 \end{aligned}$$

Exercise no. 29

Substances A and B react in independent first-order reactions to yield the same product P. The rate constants are $k_A = 2.44 \cdot 10^{-3} \text{ s}^{-1}$ and $k_B = 6.78 \cdot 10^{-4} \text{ s}^{-1}$. Consider a mixture having the initial composition $[A]_0 = 6.24 \cdot 10^{-4} \text{ M}$ and $[B]_0 = 3.42 \cdot 10^{-4} \text{ M}$. What is [P]:

a) at 1500 s

b) when $[A]_t = 1 \cdot 10^{-4} \text{ M}$

c) when $[A]_t = [B]_t$



a) At $t = 1500 \text{ s}$, the transformation rate of P is:

$$\frac{d[P]}{dt} = k_A[A] + k_B[B]$$

$$\begin{aligned} [A]_t &= [A]_0 \cdot \exp(-k_A t) = 1.63 \cdot 10^{-5} \text{ mol} \times \text{dm}^{-3} \\ [B]_t &= [B]_0 \cdot \exp(-k_B t) = 1.23 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3} \Rightarrow \end{aligned}$$

$$[A]_{1500\text{s}} = [A]_0 - x_1, [B]_{1500\text{s}} = [B]_0 - x_2$$

where x_1 is the concentration of P due to the first reaction and x_2 to the second one.

$$x_1 = 6.24 \cdot 10^{-4} - 1.63 \cdot 10^{-5} = 6.077 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$x_2 = 3.42 \cdot 10^{-4} - 1.23 \cdot 10^{-4} = 2.19 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$\text{At } 1500 \text{ s } [P] = x_1 + x_2 = 8.27 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$\text{R: b) } \frac{[A]_t}{[A]_0} = \exp(-k_A t) \Rightarrow \ln \frac{[A]_0}{[A]_t} = k_A t \Rightarrow t = \frac{1}{k_A} \cdot \ln \frac{[A]_0}{[A]_t} = 750 \text{ s}$$

$$\begin{aligned} [B]_t &= [B]_0 \exp(-k_B t) = 3.42 \cdot 10^{-4} \exp(-6.78 \cdot 10^{-4} \cdot 750) = \\ &= 2.06 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3} \end{aligned}$$

$$x_1 = [A]_0 - [A]_{750\text{s}} = 6.24 \cdot 10^{-4} - 1 \cdot 10^{-4} = 5.24 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$x_2 = [B]_0 - [B]_{750\text{s}} = 3.42 \cdot 10^{-4} - 2.06 \cdot 10^{-4} = 1.36 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$\text{At } 750 \text{ s } [P] = x_1 + x_2 = 6.6 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$[A]_t = [B]_t \Leftrightarrow [A]_0 \cdot \exp(-k_A t) = [B]_0 \cdot \exp(-k_B t) \Leftrightarrow \frac{[A]_0}{[B]_0} = \exp(k_A t - k_B t) \Rightarrow$$

$$\text{R: c)} \Rightarrow \ln\left(\frac{[A]_0}{[B]_0}\right) = t \cdot (k_A - k_B) \Rightarrow t = \frac{1}{(k_A - k_B)} \cdot \ln\left(\frac{[A]_0}{[B]_0}\right) = \frac{1}{1.76 \cdot 10^{-3}} \cdot \ln(1.82) =$$

$$= 340\text{s}$$

$$[A]_{340\text{s}} = [B]_{340\text{s}} = 6.24 \cdot 10^{-4} \cdot \exp(-2.44 \cdot 10^{-3} \cdot 340) = 2.72 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3} \Rightarrow$$

$$\Rightarrow x_1 = 6.24 \cdot 10^{-4} - 2.72 \cdot 10^{-4} = 3.52 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3} \text{ and}$$

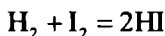
$$x_2 = 3.42 \cdot 10^{-4} - 2.72 \cdot 10^{-4} = 1.15 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

$$[P]_{340\text{s}} = x_1 + x_2 = 4.67 \cdot 10^{-4} \text{ mol} \times \text{dm}^{-3}$$

12. Seminary

Exercise no. 30

Calculate the Arrhenius factor and the rate constant for the bimolecular process:



at 700K, knowing that $E_a = 166.2 \text{ kJ/mol}$ ($E_a \cong E_{cr}$), $\varphi_{\text{orientation}} = 0.5$ and $\sigma_{\text{H}_2} \cong \sigma_{\text{I}_2} = 2 \cdot 10^{-10} \text{ m}$.

R: According to Arrhenius equation, the rate constant is:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

From the theory of collisions results:

$$A = \varphi_{\text{orientation}} \cdot \left(\frac{\sigma_{\text{H}_2} + \sigma_{\text{I}_2}}{2}\right)^2 \cdot \left(\frac{8\pi RT}{M^*}\right)^{\frac{1}{2}} \cdot N_0 \cdot \exp\left(\frac{E_a}{RT}\right)$$

where $\frac{1}{M^*} = \frac{1}{M_{\text{H}_2}} + \frac{1}{M_{\text{I}_2}}$

Since $E_a \cong E_{cr}$ is obvious that:

$$\begin{aligned} A &= \varphi_{\text{or}} \cdot \left(\frac{\sigma_{\text{H}_2} + \sigma_{\text{I}_2}}{2}\right)^2 \cdot \left(\frac{8\pi RT}{M^*}\right)^{\frac{1}{2}} \cdot N_0 = 0.5 \cdot 10^{-20} \cdot 1.7 \cdot 10^4 \cdot 6.023 \cdot 10^{23} = \\ &= 5.13 \cdot 10^7 \text{ m}^3 \times \text{mol}^{-1} \text{s}^{-1} = 5.13 \cdot 10^{10} \text{ dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1} \end{aligned}$$

$$\begin{aligned} \exp\left(-\frac{E_a}{RT}\right) &= \exp\left(-\frac{166200}{8.31 \cdot 700}\right) = 3.79 \cdot 10^{-13} \Rightarrow k = 5.13 \cdot 10^{10} \cdot 3.79 \cdot 10^{-13} = \\ &= 1.94 \cdot 10^{-2} \text{ dm}^3 \times \text{mol}^{-1} \times \text{s}^{-1} \end{aligned}$$

Exercise no. 31

The experimental values of the rate constant for a thermal decomposition (first order process) are summarized in the following table:

T / K	655	698	745
$k / 10^{-2} \text{ min}^{-1}$	0.53	6.35	67.6

1. Calculate the activation energy
2. Calculate the pre-exponential factor
3. Calculate the concentration of unreacted substance at $t = 100 \text{ min.}$ and $t = 709 \text{ K}$, if the initial concentration of reactant is $0.8 \text{ mol} \times \text{dm}^{-3}$.

R: 1. According to Arrhenius equation, the rate constant is:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

The activation energy is determined using the linear plot of $\ln k_{\text{exp}}$ vs. $\frac{1}{T}$. The slope represents $-\frac{E_a}{R}$. The experimental data will be presented as it follows:

T / K	655	698	745
$1/T / 10^{-3} \text{ K}^{-1}$	1.52	1.43	1.34
$k / 10^{-2} \text{ min}^{-1}$	0.53	6.35	67.6
$\ln k$	-5.2400	-2.7567	-0.3915

The value of slope is:

$$\frac{E_a}{R} = 26936 \Rightarrow E_a = 8.31 \cdot 26936 = 224 \text{ kJ/mol}$$

R: 2. The pre-exponential factor results from the intercept with the ordinate; $\ln A = 35.72$ with $A = 3.26 \cdot 10^{15} \text{ min}^{-1}$

R: 3. Since we deal with a first order process, the integral form of the kinetic equation can be written:

$$k = \frac{1}{t} \cdot \ln \frac{C_0}{C}$$

The $\ln k$ value corresponding to $T = 709 \text{ K}$ is -2.2170 , with $k = 0.11 \text{ min}^{-1}$.

$$\ln \frac{C_0}{C} = k \cdot t = 0.11 \cdot 100 = 11 \Rightarrow \frac{C}{C_0} = \exp(-kt) \Rightarrow C = 0.8 \cdot 1.84 \cdot 10^{-5} = 1.5 \cdot 10^{-5} \text{ mol} \times \text{dm}^{-3}$$

Exercise no. 32

A reaction has the stoichiometry: $2A + B = \text{Products}$

Time/min	[A]/M	[B]/M	[A]/M	[B]/M	[A]/M	[B]/M
0	0.100	0.100	0.100	0.200	0.050	0.10
1	0.050	0.075	0.050	0.175	0.033	0.092
3	0.025	0.0625	0.025	0.1625	0.020	0.085
9	0.010	0.055	0.010	0.155	0.009	0.080

The reaction has been followed by monitoring the concentrations of A and B at three different initial concentrations (in $\text{mol} \times \text{dm}^{-3}$).

Request: What are the reaction orders with respect to each of the reactants A and B?

R: One uses a simple form of the differential kinetic equation: $r_R = k \cdot [A]^{n_A} \cdot [B]^{n_B}$

We calculate the instant reaction rate taking into account the variation of concentration for A, respectively B.

$$r_{R_A} = -\frac{1}{2} \cdot \frac{d[A]}{dt} \cong -\frac{1}{2} \cdot \frac{\Delta[A]}{\Delta t} \quad \text{and} \quad r_{R_B} = -\frac{d[B]}{dt} \cong -\frac{\Delta[B]}{\Delta t}; \quad r_{R_A} \cong r_{R_B}$$

- For the first experiment we obtain the following data:

Time/min	[A]/M	[B]/M	$r_{R_A}/\text{mol} \times \text{dm}^{-3} \times \text{s}^{-1}$	$r_{R_B}/\text{mol} \times \text{dm}^{-3} \times \text{s}^{-1}$
0	0.100	0.100	-	-
1	0.050	0.075	0.025	0.025
3	0.025	0.0625	0.00625	0.00625
9	0.010	0.055	0.00125	0.00083

- For the second experiment:

Time/min	[A]/M	[B]/M	$r_{R_A}/\text{mol} \times \text{dm}^{-3} \times \text{s}^{-1}$	$r_{R_B}/\text{mol} \times \text{dm}^{-3} \times \text{s}^{-1}$
0	0.100	0.200	-	-
1	0.050	0.175	0.025	0.025
3	0.025	0.1625	0.00625	0.00625
9	0.010	0.155	0.00125	0.00125

- For the third experiment:

Time/min	[A]/M	[B]/M	$r_{R_A}/\text{mol} \times \text{dm}^{-3} \times \text{s}^{-1}$	$r_{R_B}/\text{mol} \times \text{dm}^{-3} \times \text{s}^{-1}$
0	0.050	0.10	-	-
1	0.033	0.092	0.0085	0.008
3	0.020	0.085	0.00325	0.0035
9	0.009	0.080	0.00092	0.00083

One can easily observe that the reaction rate does not depend on the concentration of B (varying the concentration B in the experiment 2, the reaction rate preserve the same values). Thus, the reaction order with respect to B is zero. The partial reaction order n_A is to be calculated using the data from experiment 1 and 3, knowing that:

$$\frac{(r_{t=1})_{\text{exp1}}}{(r_{t=1})_{\text{exp3}}} = \left(\frac{([A]_{t=1})_{\text{exp1}}}{([A]_{t=1})_{\text{exp3}}} \right)^{n_A^I} \Leftrightarrow \frac{0.025}{0.0085} = \left(\frac{0.050}{0.033} \right)^{n_A^I} \Rightarrow n_A^I = 2.62;$$

$$\frac{(r_{t=3})_{\text{exp1}}}{(r_{t=3})_{\text{exp3}}} = \left(\frac{([A]_{t=3})_{\text{exp1}}}{([A]_{t=3})_{\text{exp3}}} \right)^{n_A^{II}} \Leftrightarrow \frac{0.00625}{0.00325} = \left(\frac{0.025}{0.02} \right)^{n_A^{II}} \Rightarrow n_A^{II} = 2.91;$$

$$\frac{(r_{t=9})_{\text{exp1}}}{(r_{t=9})_{\text{exp3}}} = \left(\frac{([A]_{t=9})_{\text{exp1}}}{([A]_{t=9})_{\text{exp3}}} \right)^{n_A^{III}} \Leftrightarrow \frac{0.00125}{0.00092} = \left(\frac{0.01}{0.009} \right)^{n_A^{III}} \Rightarrow n_A^{III} = 2.86$$

One takes the average value of n_A ; $\bar{n}_A = \frac{2.62 + 2.91 + 2.86}{3} = 2.8 \approx 3$

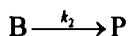
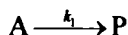
Exercise no. 33

Consider a mixture of A and B, each of which reacts independently to form the same product P. Requests:

1. Derive an equation for [P] in a mixture with initial concentrations $[A]_0$ and $[B]_0$;
2. Apply this equation to the solvolysis of a mixture of $\text{Me}_3\text{CCEt}_2\text{Cl}$ and $\text{Et}_2\text{MeCCMe}_2\text{Cl}$ in which the HCl produced was titrated as a function of time; what is the initial concentration of each? Which is which?

$t/10^3\text{s}$	0	1.8	3.6	5.4	9.0	10.8	12.6	16.2	19.8	21.6	∞
$[\text{HCl}]/10^{-2}\text{M}$	0	1.98	2.93	3.5	4.31	4.7	4.92	5.13	5.34	5.42	5.8

R: 1. We deal with the following sequence of parallel reactions:



The rates of transformation for each species are:

$$-\frac{d[A]}{dt} = k_1 \cdot [A] \Rightarrow [A] = [A]_0 \cdot e^{-k_1 t}$$

$$-\frac{d[B]}{dt} = k_2 \cdot [B] \Rightarrow [B] = [B]_0 \cdot e^{-k_2 t}$$

$$\frac{d[P]}{dt} = k_1 \cdot [A] + k_2 \cdot [B] = k_1 \cdot [A]_0 \cdot e^{-k_1 t} + k_2 \cdot [B]_0 \cdot e^{-k_2 t}$$

2. To account to the mass balance, at the end of reaction the concentration of product (HCl) is:

$$[P]_{\infty} = [A]_0 + [B]_0 = [A] + [B] + [P] = 5.8 \cdot 10^{-2} M \Rightarrow$$

$$\Rightarrow [P]_{\infty} - [P] = [A] + [B] \Leftrightarrow [P]_{\infty} - [P] =$$

$$= [A]_0 \cdot e^{-k_1 t} + [B]_0 \cdot e^{-k_2 t}$$

By logarithmation we obtain:

$$\ln([P]_{\infty} - [P]) = \ln([A]_0 \cdot e^{-k_1 t} + [B]_0 \cdot e^{-k_2 t})$$

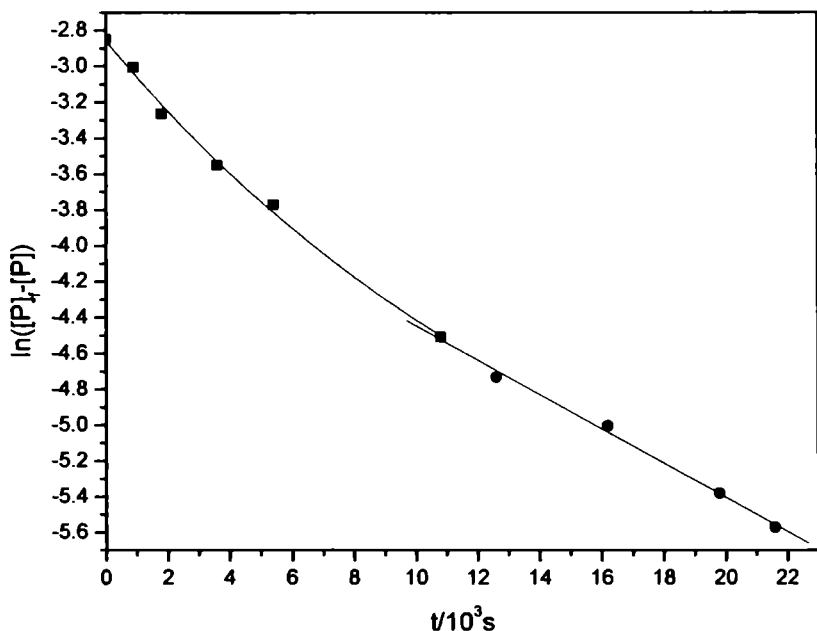
We represent $\ln([P]_{\infty} - [P])$ as a function of time:

$t/10^3 \text{ s}$	$\ln([P]_{\infty} - [P])$
0	-2.847
1.8	-3.006
3.6	-3.265
5.4	-3.551
9.0	-3.772
10.8	-4.510
12.6	-4.733
16.2	-5.006
19.8	-5.382
21.6	-5.573

The most reactive species is consumed at first. Assume that is A. At large values of time the exponential $e^{-k_1 t}$ tends to zero, so that the previous equation becomes:

$$\ln([P]_{\infty} - [P]) = \ln([B]_0 \cdot e^{-k_2 t}) = \ln[B]_0 - k_2 t$$

Thus, the rate constant for the second process k_2 and the initial concentration of B can be estimated using the linear part of the curve in the range of time 12600 – 19800 (see the figure). The slope of the linear dependence is k_2 , and the intercept is $\ln[B]_0$.



The calculated values of those two parameters are: $k_2 = 9.5825 \cdot 10^{-5} \text{ s}^{-1}$ and $[B]_0 = 3.06 \cdot 10^{-2} \text{ M}$. Knowing that:

$$[A]_0 \cdot e^{-k_1 t} = [P]_{\infty} - [P] - [B]_0 \cdot e^{-k_2 t}$$

we obtain by logarithmation the linear dependence:

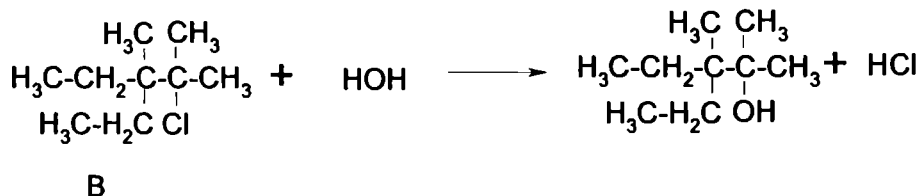
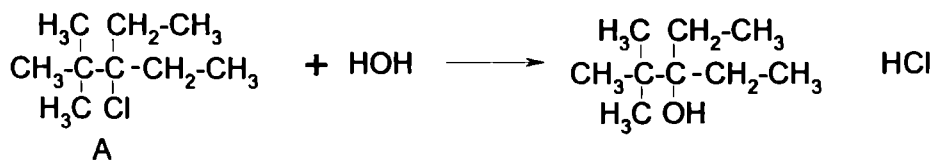
$$\ln([P]_{\infty} - [P] - [B]_0 \cdot e^{-k_2 t}) = \ln[A]_0 - k_1 t$$

where $[P]_{\infty}$, $[P]$, $[B]_0$ and k_1 are known values, summarized in the next table:

Time/s	$\ln([P]_{\infty} - [P] - [B]_0 \cdot e^{-k_2 t})$
0	-3.597
1800	-4.3861
3600	-4.958
5400	-5.347
9000	-6.222
10800	-7.932
12600	-9.501
16200	-10.4075
19800	-11.231
21600	-11.99

The slope of the straight line is $k_2 = 4.03 \cdot 10^{-4} \text{ s}^{-1}$ and the intercept is $\ln[A]_0 = -3.495$ and therefore $[A]_0 = 3.305 \cdot 10^{-2} \text{ M}$.

The equations of solvolysis reactions of the two reactants are:



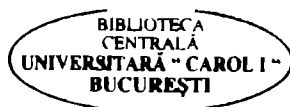
Due to the cumulate inductive effect $+I_s$ of ethyl radicals which is larger than $+I_s$ of methyl radicals, $\text{Me}_3\text{CCEt}_2\text{Cl}$ is more reactive than $\text{Et}_2\text{MeCCMe}_2\text{Cl}$.

Thus, A = $\text{Me}_3\text{CCEt}_2\text{Cl}$ and B = $\text{Et}_2\text{MeCCMe}_2\text{Cl}$.

References

1. Segal, E., Mihalcea, I., Demetrescu, I. și Mincu, G. – **Lucrări practice de Cinetica stărilor de agregare și Cinetică Chimică**, Institutul Politehnic București, Facultatea de Chimie, 1977;
2. Espenson, J.H. – **Chemical Kinetics and Reaction Mechanisms**, McGraw-Hill Inc, New York, 1995;
3. Rusling, J.F. and Kumosinski, T.F. – **Nonlinear Computer Modeling of Chemical and Biochemical Data**, Academic Press, New York 1996;
4. Pilling, M.J. and Seakins, P.W. – **Reaction Kinetics**, Oxford Science Publications, 1995;
5. Landauer, O., Petrescu, V., Geană, D., Iulian, O., Drăgănoiu, M., Meghea, A., Vișan, T., Brânzoi, V. și Ungureanu, M. – **Îndrumar lucrări practice pentru Chimie Fizică**, Institutul Politehnic București, Facultatea de Tehnologie Chimică, 1985;
6. Isac, V. și Hurdud, N. – **Cinetică Chimică și cataliză**, Ed. Știința Chișinău, 1994.

VERIFICAT
2017



**Tiparul s-a executat sub c-da nr. 1328/2004 la
Tipografia Editurii Universității din București**

620

ISBN 973575977-2



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Lei 73000